SURFACE CHEMISTRY OF SOME CONSTANT POTENTIAL SOIL COLLOIDS

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By

Johnny Ching-Win Keng

Thesis Committee:

Goro Uehara, Chairman
Tung-Ming Lai
James A. Silva

ABSTRACT

A survey was conducted to determine the extent to which the mineral compositions of soils of Hawaii consist of colloids of the constant potential type or colloids of the constant charge type. Seven soils of diverse mineralogical composition were selected for the study. They included soils with kaolinitic, oxidic, and montmorillonitic mineralogies. Three other soils which lack mineralogical designations were also examined. They included an organic soil (Histosols) and two soils developed from volcanic ash (Andepts).

Soils which contain colloids of the constant potential type were distinguished from soils which contain colloids of the constant charge type through potentiometric titration and determination of the existence or nonexistence of a well defined zero point of charge. Soils with potentiometric titration curves which intersected at a common point were judged to be colloids of the constant potential type. The point of intersection of the titration curves was used as the zero point of charge.

Organic matter, montmorillonite and a certain variety of non-crystalline alumino-silicate gave curves which did not intersect. These soils have materials which are predominantly of the constant charge type. All other soil minerals including the oxides and hydrous oxide of iron and aluminum, kaolinite, halloysite and non-crystalline hydrous oxides showed well defined zero points of charge.

On the basis of this survey, it was concluded that the majority of soils in the State of Hawaii have minerals which behave as

colloids of the constant potential type.

The implication of this finding to the soils of Hawaii and other tropical areas is discussed.

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INTRODUCTION

A useful index for characterizing the free charge for a reversible double layer system is the point of zero charge (ZPC). The surface charge σ_o is defined as

$$\sigma_o = F(Z_+\Gamma_+ + Z_-\Gamma_-)$$

where F is the Faraday constant, Z_+ or Z-, the valence and sign of the potential determining ions, and Γ_+ or Γ_+, the adsorption density of these ions. For certain types of soil colloids, for example, iron and aluminum oxides and hydrous oxides, the potential determining ions are H^+ or OH^- is equal, so the $\sigma_o = 0$.

In the absence of specifically adsorbed ions, the soil colloid is a cation exchanger at pH values above the ZPC and an anion exchanger at pH values below the ZPC.

The capacity of a soil to adsorb a particular ionic form of plant nutrient, quite clearly, would depend on whether the soil pH is above, below or at ZPC. van Raij and Peech (1972) were the first to measure ZPC of soil samples. All samples were from South and Central America. The fact that they worked with soil samples from Tropical America was not accidental. Soils high in sesquioxide and low in layer silicate content are encountered more frequently in the tropics than elsewhere. The ZPC is a useful parameter for minerals such as the oxides and hydrous oxide of aluminum, iron, manganese, silicon and titanium, and therefore for soils which contain large amount of these minerals.

Soils of the State of Hawaii are high in these oxides. For this reason, this study was undertaken to:

1. determine ZPC for a range of soils in the State,
2. determine the effect of $CaCl_2$, NaCl and Na_2SO_4 solutions on the ZPC, and
3. determine the effect of adsorbed phosphate on the ZPC.

It is hoped that attainment of the above objectives will assist researchers in interpreting cause and effect relations between soil type and soil behavior.

REVIEW OF LITERATURE

A. Surface Charge of Soil Particles

(1) The Origin of Charges

Soil mineral can be categorized into two large classes depending on the origin of the surface charge. The best known is the class called colloids with permanent charge. They are also called colloids of the constant charge type. The second class is called colloids with pH dependent charge, colloids with variable surface charge or colloids of the constant potential type.

(a) Constant Surface Charge

Imperfections in the interior of the crystal lattice of clay minerals result in an excess of net negative surface charge. Such a net charge is essentially permanent, independent of soil pH, and is responsible for the establishment of a completely polarizable double layer.

(b) Variable Surface Charge

Some soil materials acquire a surface electric charge by ionization and/or by the adsorption of specific ions.

Oxides and Hydrous Oxides: The protonation and deprotonation process on the surfaces of most oxides and hydrous oxides create a reversible interface or constant surface potential. Parks and de Bruyn, (1962) suggested that the surface charge is established by a

two-step process. Surface charge is established by adsorption of H^+ or OH^- ions. This mechanism is represented schematical in Fig. 1 and Fig. 2.

Broken edges: Edges of clay minerals may also be either positively or negatively charged as indicated in Fig. 3 as suggested by Schofield and Samson (1953). This figure shows that the atomic groupings at the edges are occupied by Mg or Al in octahedral positions and Si in tetrahedral positions, and the sign and magnitude of the charge are determined by pH.

Humus: Soil humus acquire its charge mainly through the ionization of carboxyl ($-COO^-$) and amino groups ($-NH_3^+$). The ionization of these groups depends on the pH of the soil solution (Bremner, 1956).

(2) Density and Distribution of the Charge

More than 80% of the electrical charges of soil are located on particles which are less than 2 mm in diameter. An average value of the charge density can be derived from the exchange capacity and the surface area per unit mass of colloid (van Olphen, 1963). Bower (1959) and Pratt, et al. (1962) report that the surface charge densities of most soils fall between 1 to 3.5 10^{-7} meq/cm^2 in the range of pH 5 to pH 8.

(3) Chemical Composition and Interrelations

It is generally believed that clay minerals and humus are the main contributors of negative charges of soil colloids (Grim, 1953; Bremner, 1956; and Pratt, 1961)

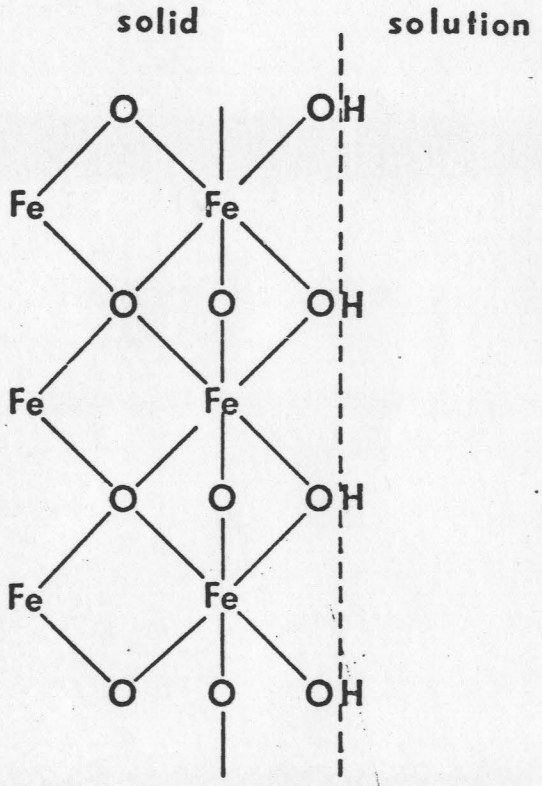

Fig. 1. Schematic Illustration of an Uncharged Hydrated Ferric Oxide Surface

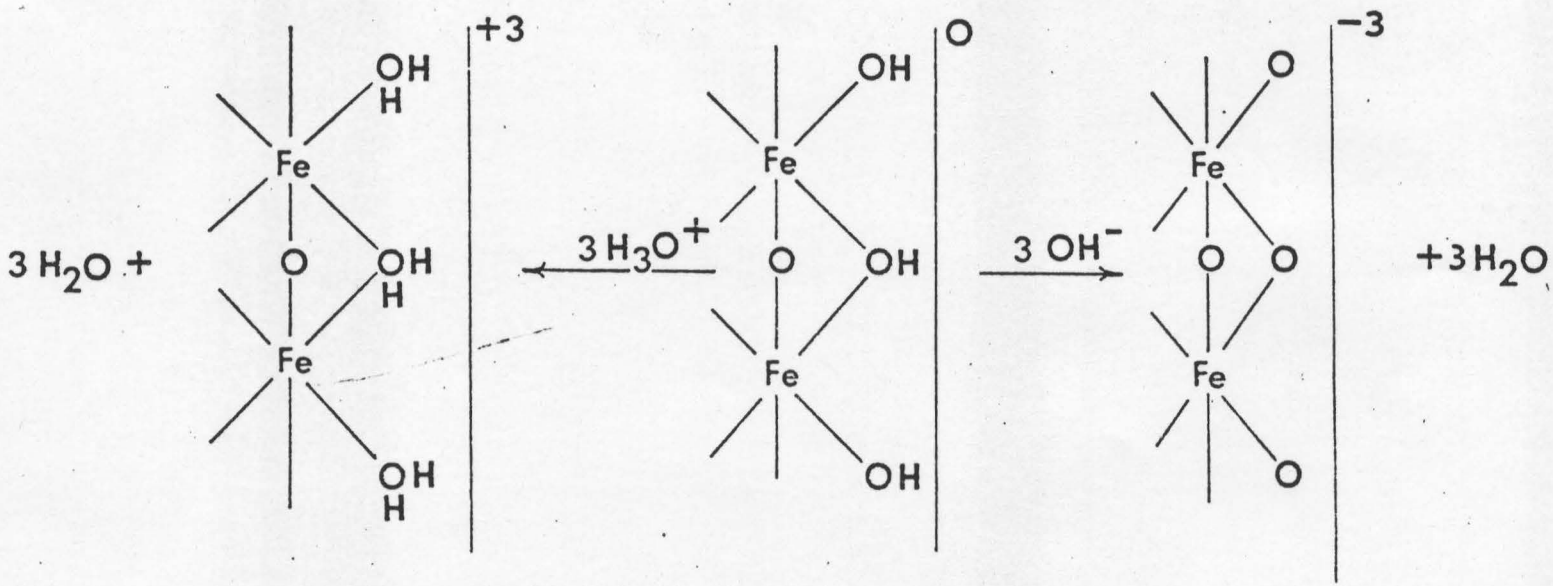

Fig. 2. The Mechanism of Adsorption and Dissociation of H^+ and OH^- Ions

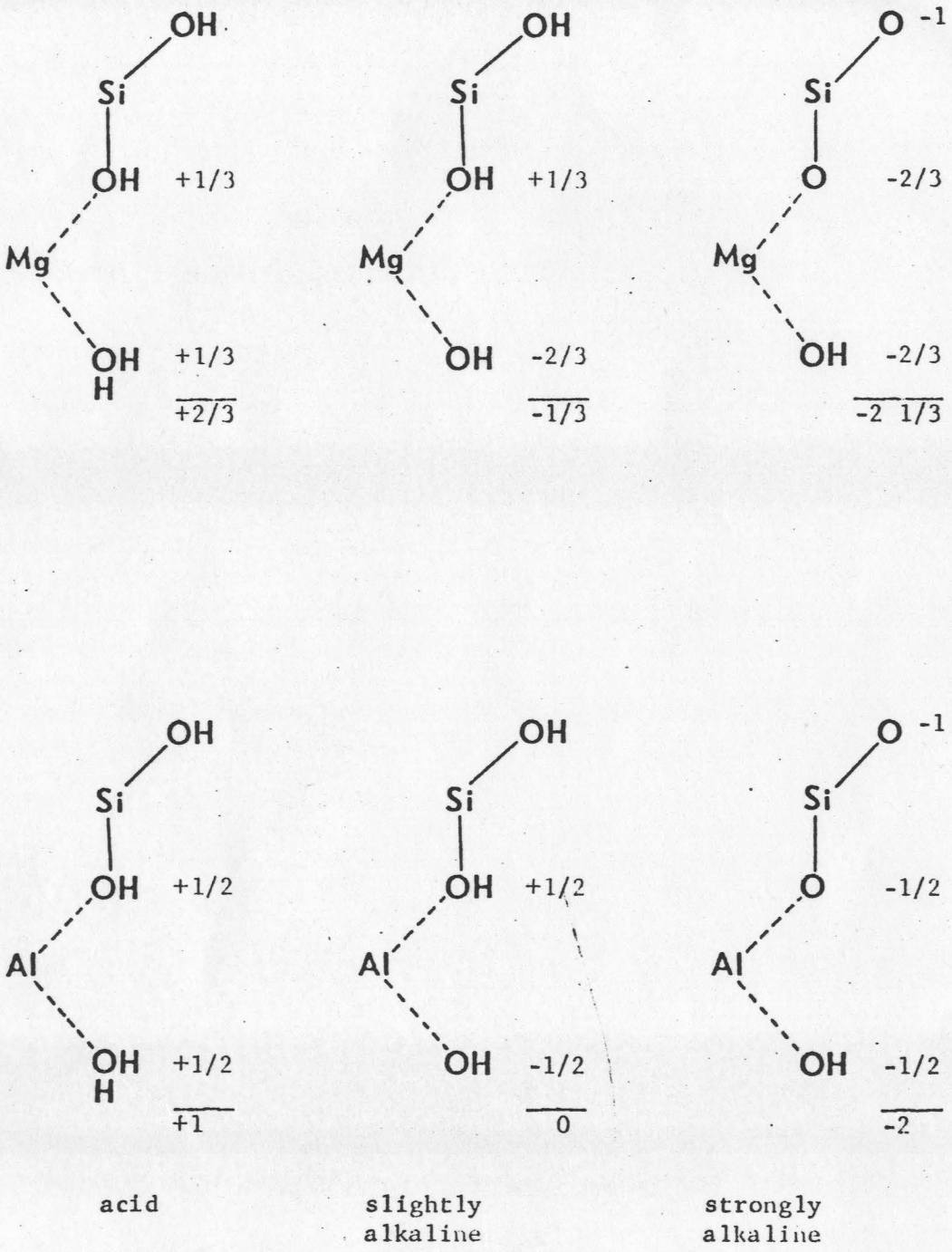

Fig. 3. The Charges on the Edges of Clay Particles Under Acid and Alkaline Conditions as Affected by Mineralogical Composition

while oxides and hydrous oxides are the major sources of positive charges. The $-NH_2$ group of humus can also contribute to positive charges at low pH. The sum of the negative charges of organic-inorganic compounds is less than the sum of the negative charges measured individually (Sen, 1960). Similar results have been obtained by Scheffer and Ulrich (1960), Alexandrove (1960), and Broadbent (1952). This suggest that a strong interaction exists between the organic and inorganic components of soil (Deuel, 1960 and Greenland, 1971).

Mattson and Hester (1935) noted that adsorption of phosphate increased the surface negative charge. Onikura (1959, 1960) and Mehlich (1960) also show that adsorption of silicate and phosphate increases net negative charge of soil colloids by 10 to 50%.

B. Electrical Double Layer

The electrical double layer at the solid-solution interface is constituted by the surface charge and its counter charge in the solution. Any description of the electrical double layer amounts to formulating the distribution of charge and potential. The classical Gouy-Chapman-Stern-Grahame (GCSG) model of the electrical double layer and a very recently proposed "porous double layer" concept (Lyklema, 1968) will be discussed in this thesis, as well as the concept of "double diffuse double layer" (Breeuwsma and Lyklema, 1971).

(1) The Gouy-Chapman-Stern-Grahame Model

Models of the double layer go back to Helmholtz (1879)

who suggested a double layer model analogous to a electrical capacitor. The first detailed model is due to Gouy (1910) and Chapman (1913), who independently gave an analysis which starts with the same premises as the Debye-Huckel theory (1923). Stern (1924) modified the Gouy-Chapman model after a consideration of the compact double layer and reintroduced the concept of specific adsorption. Grahame (1947) suggested that specifically adsorbed ions might develop two distinct layers of closest approach. The inner plane of closest approach (inner Helmholtz plane, or IHP) within which anions can approach the electrode, and the outer plane of closest approach (outer Helmholtz plane, or OHP) within which the cations approach the electrode. The Gouy-Chapman theory is applicable to the region beyond the outer plane, that is, the diffuse double layer.

Figure 4 shows the three important features of the GCSG model. Fig. 4-a shows a diffuse (Gouy) layer, in which the free energy of adsorption per ion, ΔG_{ads}, is completely determined by the electrostatic interaction between the ion and the surface. This describes the situation wherein no specific adsorption occurs. Fig. 4-b presents the Stern model of double layer. Following Grahame (1947), the plane through the centers of the purely electrostatically adsorbed ions nearest to the surface is called the OHP. The OHP and the solid surface is the compact layer, in which the ions must be specifically adsorbed by some chemical interaction with the surface

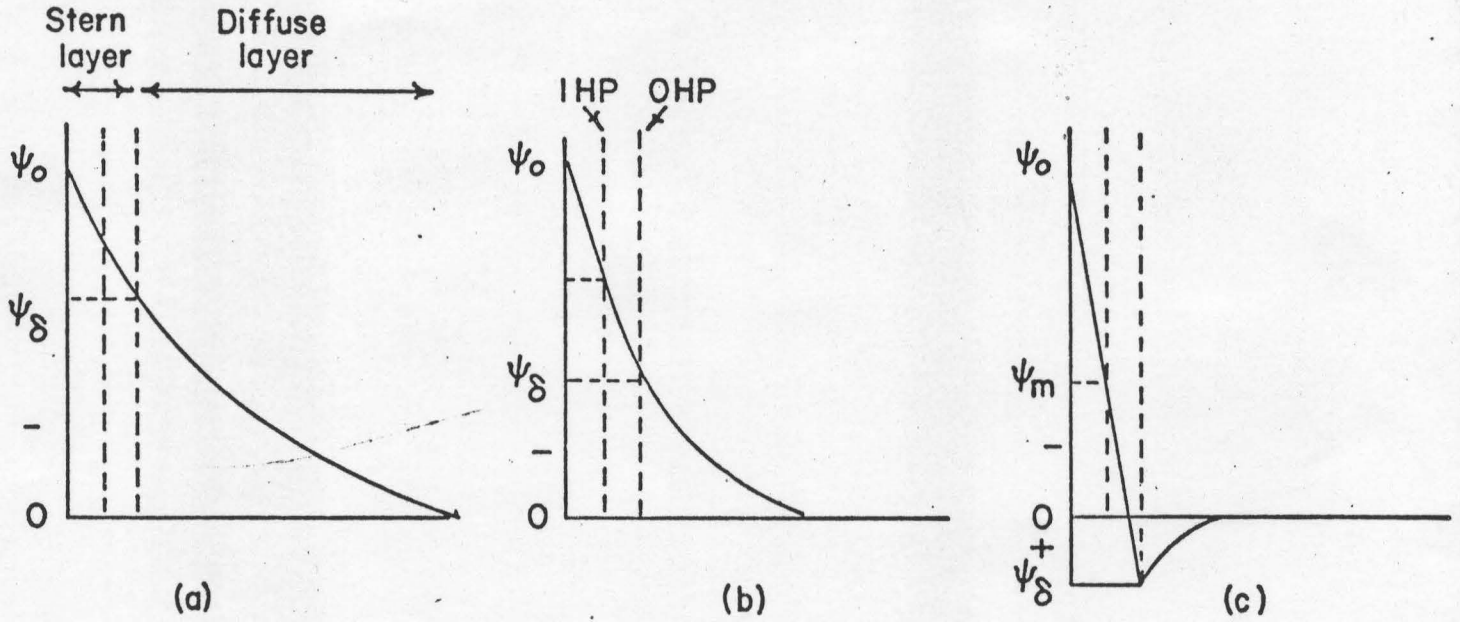

Fig. 4. Potential and Charge Distribution in the Double Layer According to the GCSG Model (Source: Breeuwsma, 1973)

charge. The plane through the center of specifically adsorbed ions is referred to the IHP. Fig. 4-c shows a charge reversal against the surface in the compact layer associated with superequivalent adsorption of ions. The term super-equivalent adsorption has been defined by Lyklema (1968).

(2) Mathematical Treatment

An exact mathematical treatment of the electrical double layer is a complex and difficult problem (Kruyt, 1952 and Delahay, 1965). For simplicity those two kind of double layer, spherical and plane surface double layers, which will be discussed below are assumed to consist of a negative, uniformly charged surface of infinite extent in contact with solution phase containing positive and negative ions. The solution is assumed to influence the double layer only through its dielectric constant.

For a reversible double layer system the surface charge "σ" may be expressed by the relation

$$\sigma = F (Z_+\Gamma_+ + Z_-\Gamma_-) \qquad (1)$$

where F is the Faraday constant; Z_+ (or Z-), the valence including the sign of the electrical charge, and Γ_+ (or Γ_-), the adsorption density of potential determining ionic species.

In the presence of specific adsorption, the relation is given by:

$$\sigma = \sigma_s + \sigma_d \qquad (2)$$

where σ_s and σ_d refer to the charge densities in the compact and diffuse layer, respectively.

If the adsorbed potential determining ions are H^+ and OH^-, the surface electric potential due to charges is determined by the pH of the equilibrium solution and is given by Nernst type relation.

$$\psi = (RT/F)\ln(H^+/H^+_{zpc}) = 59\ (ZPC-pH)mv \quad \text{at } 25^oC \tag{3}$$

Thus, it should be possible to calculate the double layer potential at any pH value if the ZPC is known.

Expressions for σ_d is, based on the poisson's equation and the Boltzmann distribution law, given by the Gouy-Chapman theory of a flat surface double layer as:

$$\sigma_d = (2\eta D\kappa T/\pi)^{\frac{1}{2}} \sinh\ (Ze\psi_\delta/2\kappa T) \tag{4}$$

Equation 4 can be reduced to

$$\sigma_d = \frac{DK}{4\pi}\psi_\delta \tag{5}$$

if $Ze\psi_\delta << Kt$, and where $K^2 = \frac{8\pi e^2 n_o z^2}{D\kappa T}$ D is the dielectric constant of the medium, Z is the valence of the counter ion, n_o is the concentration of the equilibrium solution in number of ions per cm^3, T is the absolute temperature, κ is the Boltzmann constant, and ψ_δ is the electric potential at the boundary between the compact layer and the diffuse layer.

From Eq. (5), it can be seen that ψ_δ depends both on the charge density of the diffuse layer (σ_d), and on the ionic composition of the solution through K. $1/\kappa$ is customarily referred to as the "thickness" of the diffuse double layer.

The charge density for the compact layer is given by

Stern (1924)

$$\sigma_s = N_1 Ze/[1+(N_A/M_n)\exp 1-(Ze\psi_s-\phi)/KT)] \quad (6)$$

in which N_1 is the number of adsorption sites per cm^2 of the surface, N_A is Avogadro's number, M is the molecular weight of the solvent, and ϕ is the specific adsorption potential of the counter-ions at the surface. The surface charge is also given by the equation for a molecular condenser

$$\sigma = (D/4\pi\delta)\ (\psi_o-\psi_s) \quad (7)$$

where D is the dielectric constant of the medium in the field of the molecular condenser, and δ is the thickness of the Stern layer.

Loeb et al. (1961) developed a theory for spherical double layers. Which is adequate in calculating the diffuse double layer for spherical particles when $Ka < 20$, where a is the particle radius. In their work, they introduce the concepts of reduced potential y, $(y = \frac{e\psi}{KT})$, and reduced distance q, $(q = \frac{K\gamma}{\lambda})$. Where $\lambda^2 = \frac{Z_+ + Z_-}{2Z}$ and $K^2 = \frac{4\pi e^2 C\ N_A(Z_+ + Z_-)}{1000\ DKT}$, c is the molar concentration and Z_+ (or Z_-) is the valence. The charge density is expressed as

$$\sigma = \frac{DKTK}{4\pi e\lambda}\ (I) \quad (8)$$

where I is a function of the reduced potential y, and the reduced distance q. The thickness of the double layer d is expressed as

$$d = \frac{1}{K}\ \frac{ay_o}{q_o I_o - y_o} \quad (9)$$

where

$$y_o = \frac{e\psi_o}{KT},\ q_o = \frac{Ka}{\lambda}$$

The soils under study, however, usually contain a predordernance of particles with Ka values larger than 20. The flat surface double layer equation is adequate for the

colloid considered in this study.

(3) Zero Point of Charge and Iso-Electric Point

In a reversible surface charge colloidal system, the zero point of charge (ZPC) is defined as the pH value for which $\Gamma_{H^+} = \Gamma_{OH^-}$. Following the use of the traditional adsorption method, the ZPC coincides with the intersection of the surface charge-pH curves for different ionic strength where there is no net adsorption of ions at the ZPC. When specific adsorption occurs, the ZPC will shift.

The Iso-Electric Point (IEP) is defined as the point with equal rate of ion adsorption and desorption, in other words, IEP represents the point of zero electrokinetic potential. In the absence of specific adsorption, the ZPC and IEP are interchangeable. But they move into opposite directions when specific adsorption occurs at the ZPC (Lyklema, 1971). For example, in the case of super-equivalent adsorption of cations, the surface charge σ is negative but at the same time, ψ_d is positive, and the surface charge must be lowered by raising the pH, to bring the electrokinetic potential back to zero.

(4) Porous Double Layer Model

The GCSG model and it's modifications were mainly based on experiments with mercury or silver iodide interface. Certain oxides, however, behave quite differently. Tadros and Lyklema (1968 and 1969) pointed out that for precipitated silica, the high surface charges may be due to penetration of ion into the solid. Lyklema (1971) has also shown that for silica the surface charge increases with increasing

degree of nitrogen porosity. Thus, a porous double layer model was proposed and a quantitative elaboration of it was given by Lyklema (1968). Lyklema's paper has shown some interesting features. His studies show that with increasing surface charge the quantity $\sigma - \sigma_s$ i.e. the charge effective in colloid stability, soon become independent of σ even at low penetration depths ($\sim 1\text{Å}$). In other words, at high surface charge further adsorption of potential determine ions is completely compensated for by adsorption of counterions inside the solid. His studies also indicate that the counter-ion penetration (both potential determining ions and counter-ions) is much more sensitive toward the penetration depth than to variations in solute concentration. This could mean that the size of counterion and the pores are more important in counterion adsorption than the concentration and specific adsorption potential of the counterions.

Another interesting deviation from mercury or AgI studies is the shape of $\sigma - \psi$ curves. In mercury and AgI the $\sigma - \psi$ relation is concave with respect to the axis, but in oxides the curves are convex. This has important implications in liming of Tropical soils.

MATERIALS AND METHODS

A. Characterization of Samples

Seven soils were used in this study. They are classified according to USDA Soil Taxonomy (1970) as Typic Gibbsihumox (Halii series), Typic Torrox (Molokai series), Typic Hydrandepts (Hilo series), Typic Tropofolist (Puna series) Typic Eutrandepts (Waimea series), Typic Chromusterts (Lualualei series), and Humoxic Tropohumults (Paaloa series). In all, fourteen samples were selected from the above soils including, in some cases, more than one horizon from a given soil profile. Some properties of the soils are listed on Table 1. Four mineral samples were also selected for study. They were gibbsite nodules from a Gibbsihumox, iron oxide from a iron stone sheet collected from deep colluvium on Nuuanu Pali, Oahu, Hawaii, Kaolinite (Bath, South Carolina) and Montmorillonite (Wyoming Bentonite). X-ray diffraction tracings of soils and minerals are presented in Appendix A.

B. Pretreatment of Samples

All samples except the Hilo soil (Typic Hydrandepts), were air dried and ground with a wooden pestle to pass through a 20 mesh sieve. A portion of the Halii surface soil was passed through 100 mesh sieve to measure the effect of grinding on ZPC. The Hilo soil samples were determined without prior sieving. No washing process were applied to the samples for the determination of potentiometric titration curves, and every effort was made to maintain soil conditions encountered in the field.

Table 1. Selected properties of soils

Series	Soil Sample Family	Subgroup	Depth (inch)	Organic C %	C.E.C. (NH_4OAc)	pH H_2O	pH KCl	Mineralogical Composition (%) Goethite & Hematite	Gibbsite	Kaolinite
Halii	clayey ferritic isothermic	Typic Gibbsihumox	0-5	10.90	33.33	4.6	4.5			
Halii	clayey ferritic isothermic	Typic Gibbsihumox	24-36			5.2	5.4			
Molokai	clayey kaolinitic isohyperthermic	Typic Torrox	0-6	1.92	23.50	5.7	5.0		12	40
			24-36	0.50	14.40	6.6	5.9		10	54
Hilo	thixotropic isohyperthermic	Typic Hydrandepts	0-6	5.30	67.60	5.8	5.6	27	30	
			25-40	2.90	57.10	6.3	6.3		30	
Paaloa	clayey oxidic isothermic	Humoxic Tropohumults	12-24	0.95	7.60	4.7	4.4	50	35	
Waimea	medial isothermic	Typic Eutrandepts	12-24	9.55	52.64	6.2	5.7			
Puna	euic isothermic	Typic Tropofolists	0-5	20.00						
Lualualei	very fine montmorillo-nitic isohyperthermic	Typic Chromusterts	12-24	0.42	32.90	7.5	5.4			

In addition, the samples from the Halii subsoil were treated with 5,000 and 10,000 ppm of P as NaH_2PO_4 and $CaHPC_4$ respectively. The treated samples were stored in plastic bags and allowed to equilibrate for six weeks with occasional mixing.

C. Potentiometric Titration Curves

A measured volume of standard acid or base was added to a known amount of sample suspended in a solution of an electrolyte. When the system reached equilibrium, the pH was measured. A blank test, i.e. and equal volume and concentration of the same electrolyte and acid or base without soil or mineral was also carried out. The quantity of the potential determining ions adsorbed was calculated from the difference in the amount of potential determining ions necessary to produce the same change in pH of the blank. The ZPC was taken to be the common intersection point of the titration curves carried out in the presence of different concentration of the same electrolyte. The surface charge, σ, was derived from Eq. (1). The above method generally follows the technique described by van Raij and Peech (1972).

Procedure

To a 4 gram sample suspended in an electrolyte solution in a 50 ml beaker, appropriate amounts of 0.1 N HCl or 0.1N NaOH solution were added. The electrolyte solutions were NaCl, $CaCl_2$ and Na_2SO_4. The total volume was made up to 20 ml with distilled water, and the final concentrations of each electrolyte were sealed with a piece of parafilm.[1/] After 4 days of equilibration

[1/] Although dissolved CO_2 is known to have an effect on the titration curves, no attempt was made to exclude CO_2. It was reasoned that since CO_2 was a natural part of soil solution, the data would represent real soil systems more accurately with CO_2.

(see next section), the pH was determined. A Beckman research pH meter was used. The data were processed and plotted through the University of Hawaii Computer Center.

D. Relative Adsorption Density vs. Time

An additional test to determine adsorption rate was conducted. A series of material from a Halii subsoil were used for this purpose. Following the procedure of the proceeding section, the pH was measured every 15 minutes in the first hour, and then, was measured every several hours until the 7th day. The results show that about two and a half days are required to stabilize pH readings in 1N solution. In all other concentration, equilibrium was reached after 100 hours (Fig. 5 and Fig. 6). On the basis of these results, a 4-day equlibrium time was chosen.

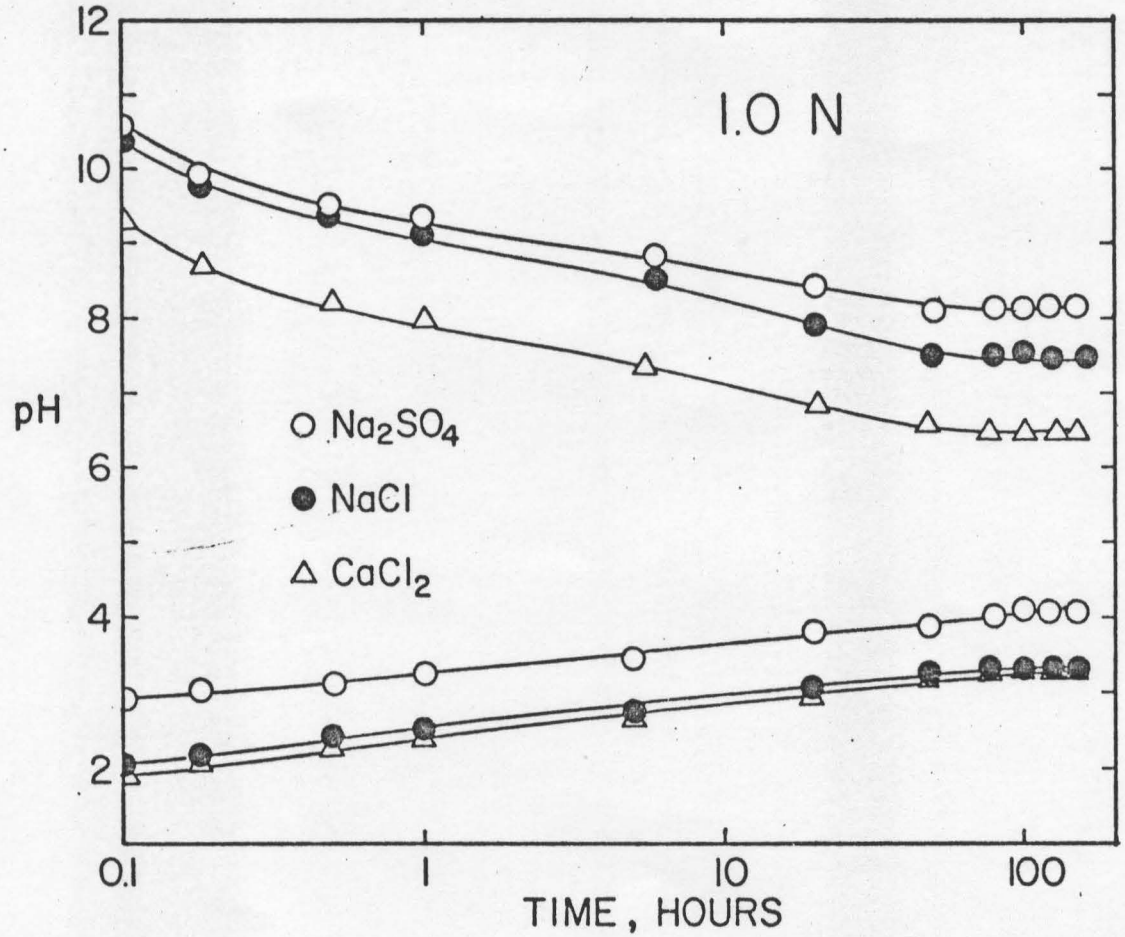

Fig. 5. The Change in pH with Time after Addition of Acid or Base in 1.0N $CaCl_2$, NaCl and Na_2SO_4

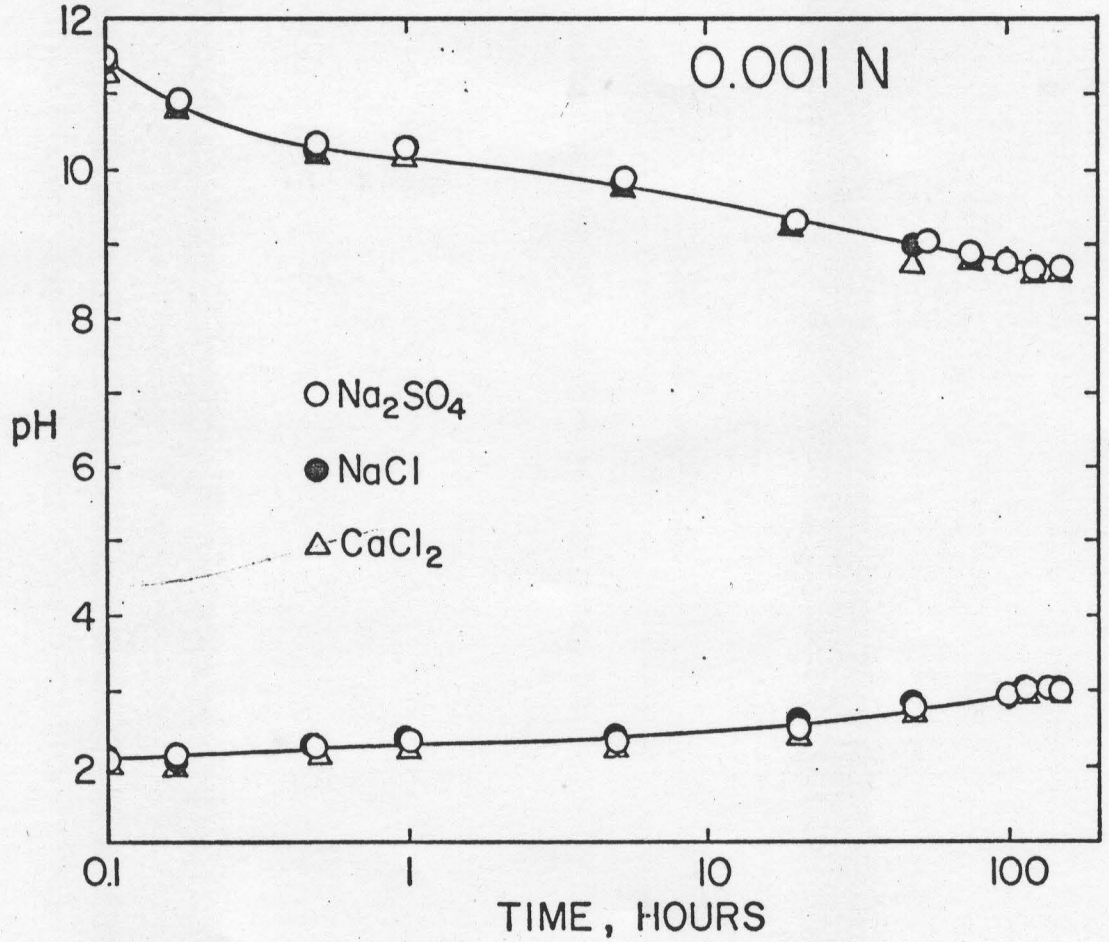

Fig. 6. The Change in pH with Time after Addition of Acid or Base in 0.001N $CaCl_2$, NaCl and Na_2SO_4

RESULTS AND DISCUSSION

A. Kinetics of Adsorption

Fig. 5 and Fig. 6 show the effect of time on pH upon addition of acid or base. The time variable is plotted on logarithmic scale. An abrupt change in pH was observed within the first hour, and subsequently the rate of change diminished with time until virtual equilibration was attained after 100 hours.

An interesting feature in Fig. 5 and Fig. 6 is that deprotonation appears to occur in two steps. The first occurs in the first hour and the second becomes apparent after five hours. This two-step (fast and slow) adsorption process was attributed by Onoda and de Bruyn (1966) to the rapid redistribution of protons at the interface of the solid particle and the solution phase, followed by the slow diffusion of protons through the hydrated interfacial region. Uehara and Jones (1973) show that this interfacial region consists of an amorphous coating. Breeuwsma (1973) has also observed a similar surface condition on hematite and refers to the surface as "porous" after Lyklema (1968). Breeuwsma (1973), however, believes that the two-step reaction is only apparent. He feels that unless the system is free of CO_2, the second step will always occur.

B. Effect of Grinding on Adsorption Density

A comparison of adsorption density of H^+ and OH^- was made on the Halii surface material which had been passed through 20 mesh and 100 mesh sieves. As shown in Table 2 and Table 3, the values of ZPC and the zero point of titration for these two

Table 2. The ZPC determined in $CaCl_2$, NaCl, and Na_2SO_4 solutions

Soil Sample	Depth (inch)	Zero Point of Charge in $CaCl_2$	NaCl	Na_2SO_4
Halii Series	0-5	4.18	4.50	5.80
	0-5[a/]	4.20	4.66	5.80
	24-36	5.59	6.00	6.50
Molokai Series	0-6	4.23	4.68	5.65
	24-36	4.70	4.90	6.50
Hilo Series	0-6	4.48	4.79	5.60
	25-40	5.78	6.35	7.10
Paaloa Series	12-24	3.56	3.77	4.20
Waimea Series	12-24	--	--	5.95
Puna Series	0-6	--	--	--
Lualualei Series	12-24	--	--	--
Mineral Sample				
Goethite		5.28	5.54	6.68
Mixture of Gibbsite & Halloysite		4.20	4.60	6.40
Kaolinite		--	--	4.10
Smectite		--	--	--

Note: Values after " " are estimated values, owing to lack of well defined intersection of titration curves.

[a/] Halii soil ground to pass 100 mesh screen

Table 3. The zero point of titration measured in different concentration of $CaCl_2$, NaCl and Na_2SO_4

Sample Source	Depth (inch)	Zero Point of Titration (pH)											
		$CaCl_2$				NaCl				Na_2SO_4			
		1N	0.1N	0.01N	0.001N	1N	0.1N	0.01N	0.001N	1N	0.1N	0.01N	0.001N
Soil Samples													
Halii	0-5	4.30	4.48	4.69	4.79	4.60	4.67	4.78	4.81	5.10	5.12	4.92	4.73
Halii[a/]	0-5	4.33	4.59	4.68	4.79	4.73	4.80	4.89	4.96	5.29	5.38	5.30	4.99
Halii	24-36	5.15	5.58	5.36	5.30	5.45	5.55	5.53	5.26	6.41	6.22	6.21	5.98
Molokai	0-6	5.04	5.35	5.82	6.04	5.37	5.70	6.08	6.14	5.93	6.05	6.11	6.39
Molokai	24-36	5.44	5.78	6.06	6.40	5.91	6.13	6.18	6.32	6.48	6.51	6.47	6.44
Hilo	0-6	4.43	4.56	4.56	4.63	4.67	4.80	4.82	4.75	5.23	5.30	5.46	5.13
Hilo	25-40	5.67	5.89	5.97	5.84	6.12	6.26	6.23	6.11	6.64	6.74	6.68	6.36
Paaloa	12-24	3.79	3.88	3.98	4.30	3.87	4.02	4.24	4.43	4.33	4.31	4.38	4.52
Waimea	12-24	5.14	5.58	5.96	6.13	5.59	5.91	6.02	6.13	6.01	6.06	6.13	6.16
Puna	0-6	5.36	5.76	6.07	6.20	5.79	5.98	6.07	6.20	6.16	6.12	6.16	6.15
Lualualei	12-24	7.07	7.39	7.79	8.22	7.43	7.62	8.01	8.22	7.99	7.75	8.01	8.28
Mineral Samples													
Goethite		4.92	4.92	4.81	4.68	5.16	5.14	4.99	4.96	5.85	6.20	6.31	5.50
Gibbsite and Halloysite		4.98	5.14	5.15	5.28	4.98	5.12	5.28	5.48	5.69	5.90	5.87	5.51
Kaolinite		3.88	3.89	4.06	4.46	3.86	4.18	4.58	4.88	4.51	4.41	4.76	5.06
Smectite		7.75	7.96	8.98	9.38	8.37	8.76	9.26	9.39	8.81	8.85	9.30	9.31

[a/] Halii soil ground to pass 100 mesh screen

particle sizes are indistinguishable, but when one compares the σ_o -pH curves in Fig. 12 and Fig. 13, it is easy to see that the finer particles possesses a higher buffering capacity. This suggests that there is no change in the surface nature of the material before or after grinding, but larger surface area in the finer particles results in higher adsorption density per unit weight of sample.

C. ZPC of Minerals

Unlike the highly purified monomineralic samples generally used in laboratory studies, soil materials generally contain more than one mineral. If each mineral in the soil sample possesses a well defined ZPC, the ZPC of a mixture will fall between the ZPC's of those minerals with the highest and the lowest values. If the mineral surface in this mixture remains uncontaminated, and the extent of ionization is negligible (Parks, 1967) the ZPC of the mixture ZPC_m will be:

$$ZPC_m = X_1ZPC + X_2ZPC + X_3ZPC + ...$$

where X refers to the weight fraction of each mineral and the subscript identifies the mineral. This simple relation probably never applies since surfaces generally become contaminated in mixed systems. Even in soil materials containing several minerals, Jones and Uehara (1973) show that most soil minerals are coated with a thin gelatinous film. Their finding suggests that the ZPC of soils may in fact be the ZPC of this coating.

Having said this, potentiometric titration of several monomineralic samples were analyzed for their ZPC's (Figs. 7, 8, 9, 10, and 11). The minerals were goethite, gibbsite, kaolinite

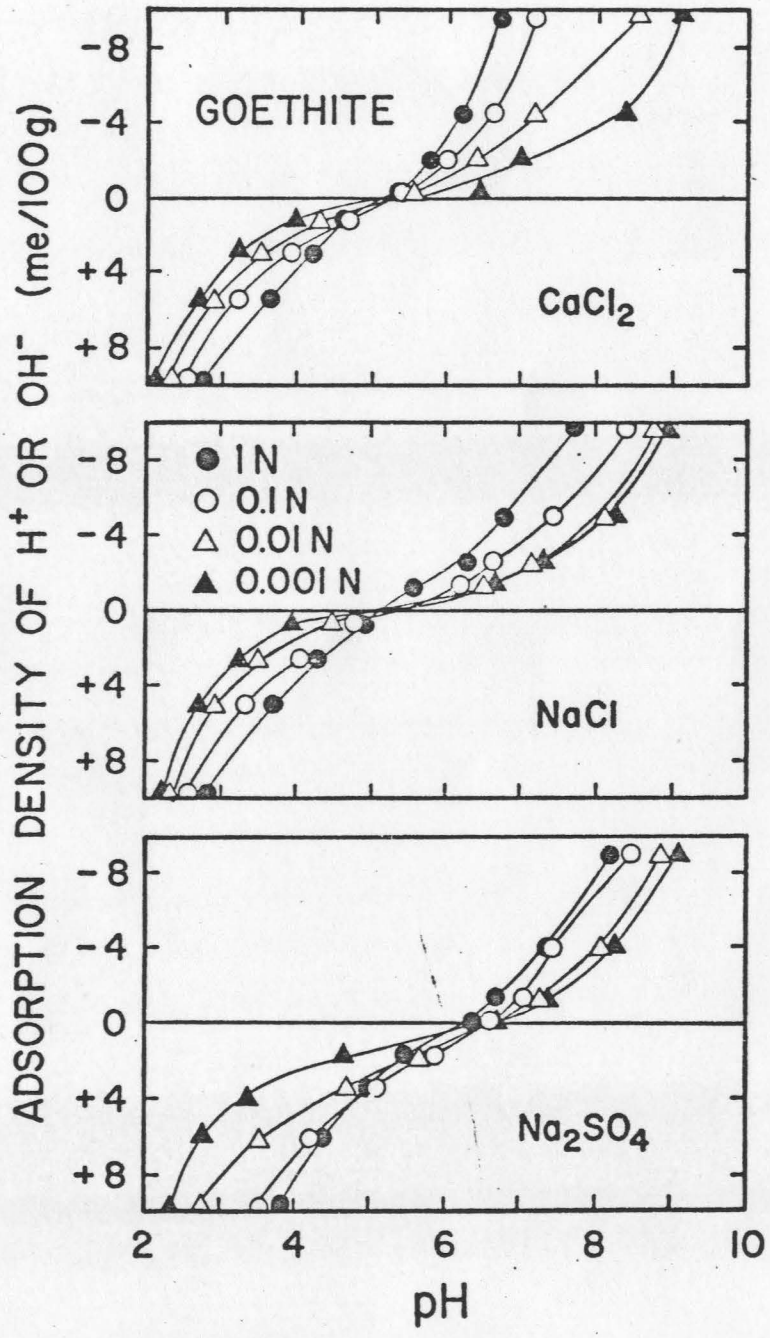

Fig. 7. The Net Electric Charge of Goethite as Determined by Potentiometric Titration

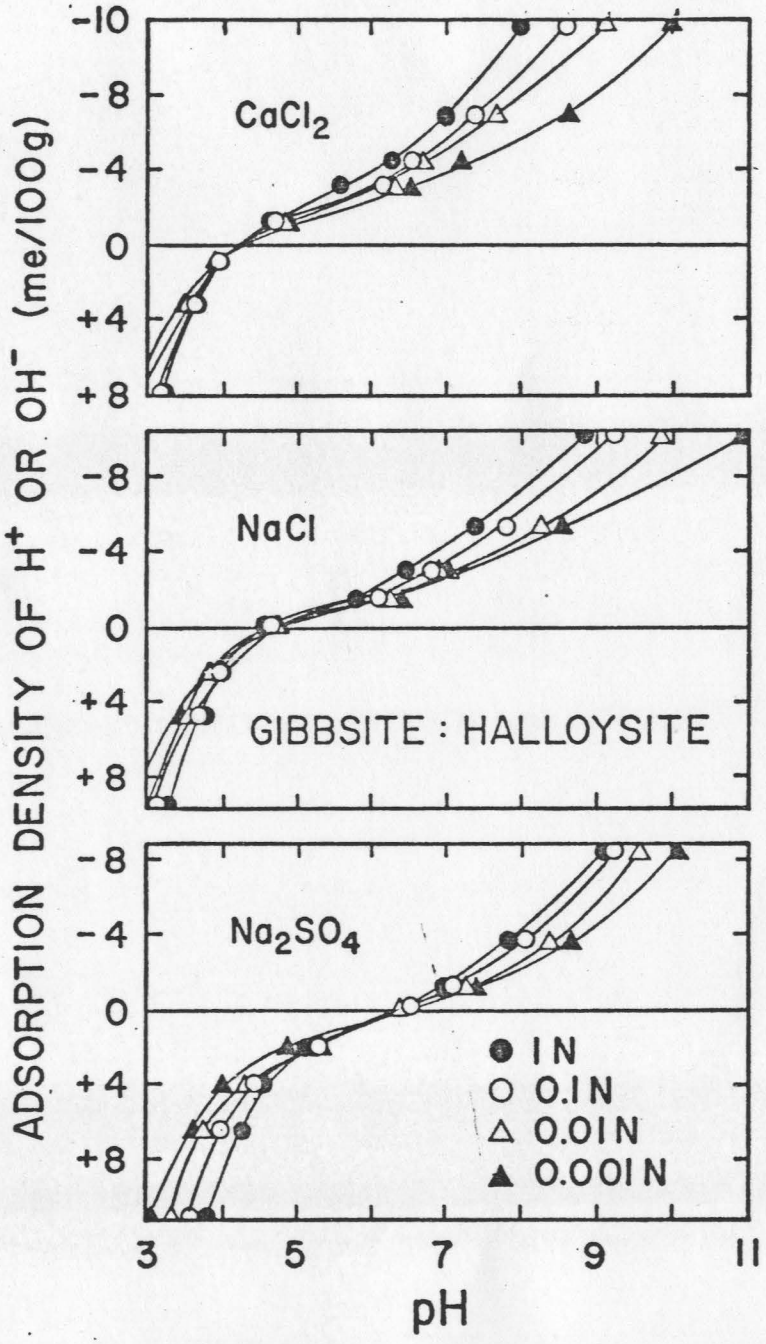

Fig. 8. The Net Electric Charge of a Mixture of Gibbsite and Halloysite (Hawaii) as Determined by Potentiometric Titration

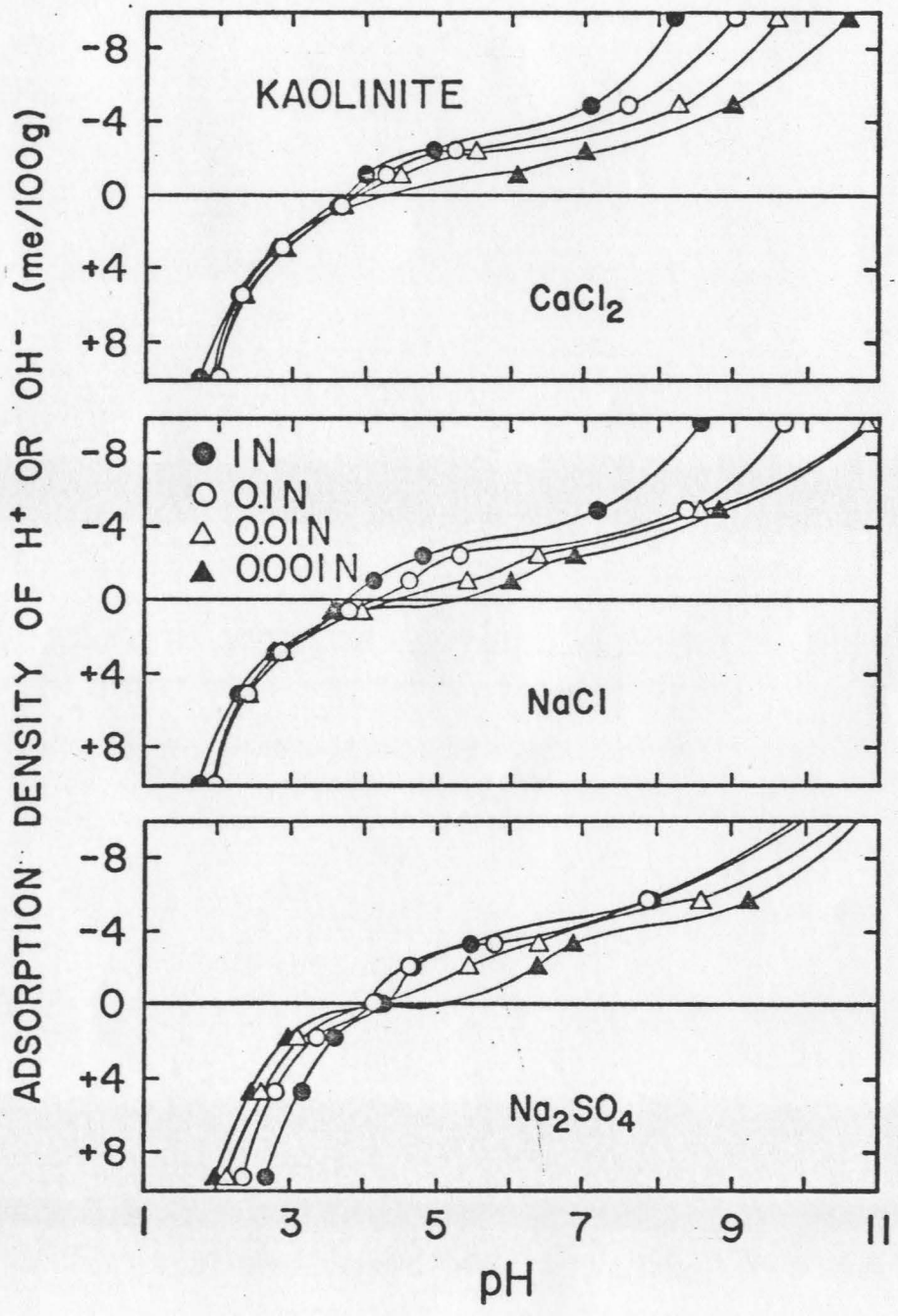

Fig. 9. The Net Electric Charge of Kaolinite Mineral as Determined by Potentiometric Titration

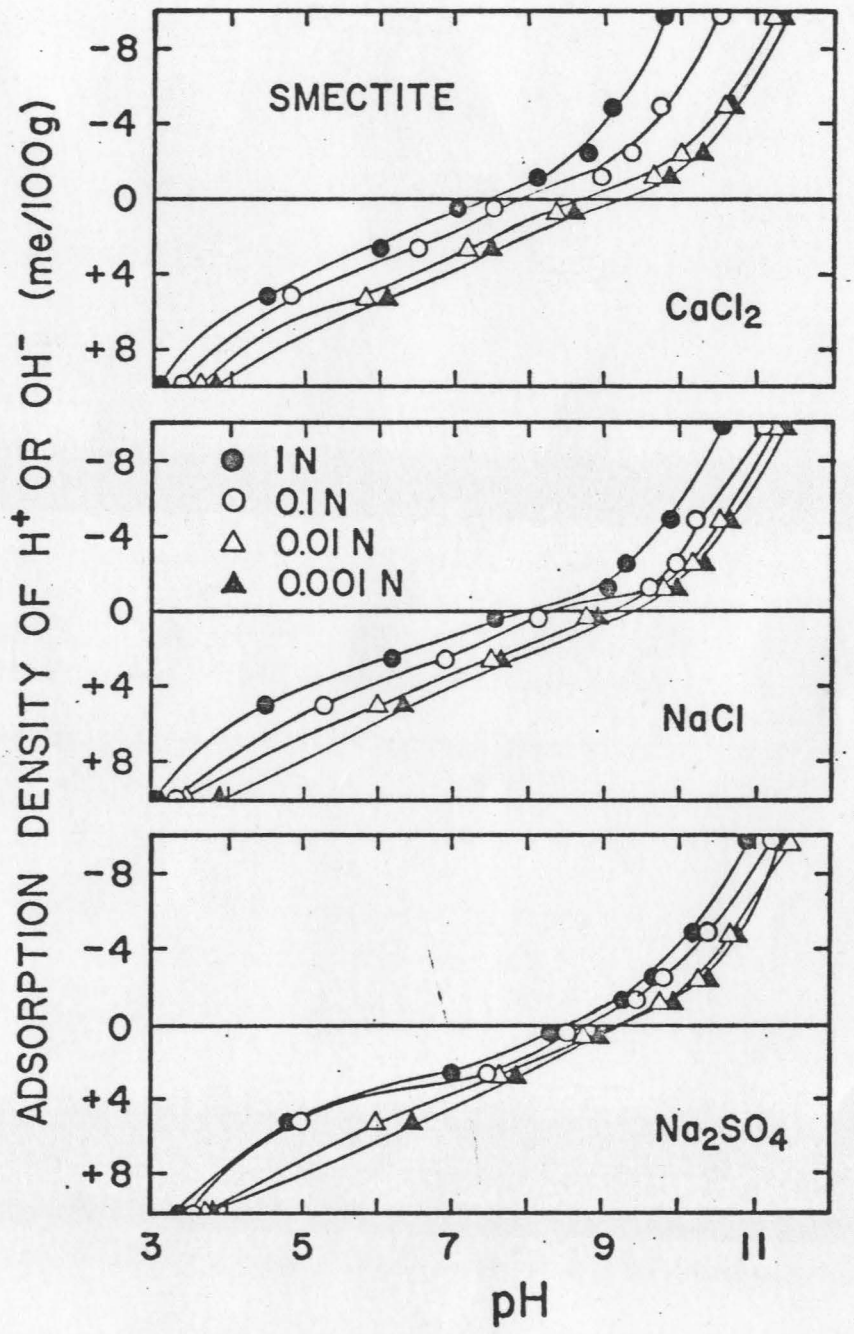

Fig. 10. The Potentiometric Titration Curves for Montmorillonite Mineral (Wyoming Bentonite) as Determined by Potentiometric Titration

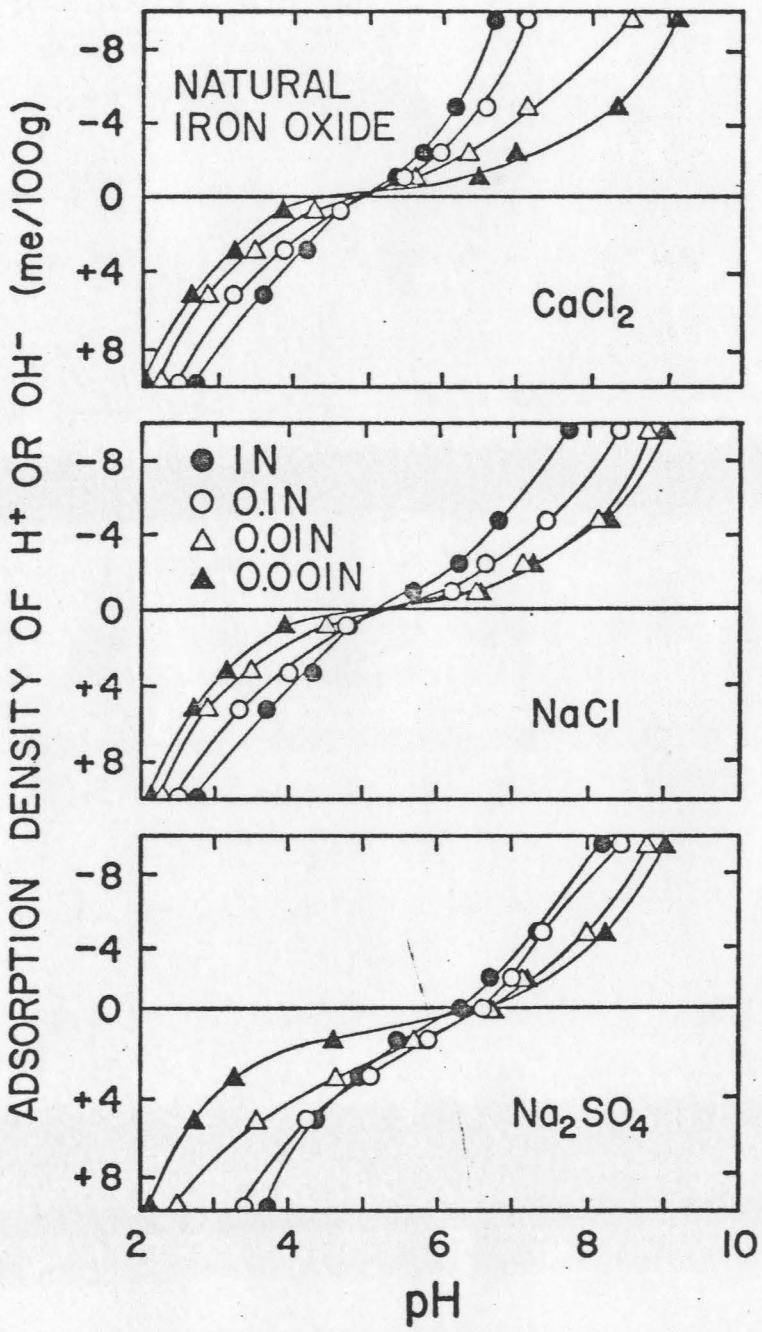

Fig. 11. The Net Electric Charge of Natural Iron Oxide (Hawaii) as Determined by Potentiometric Titration

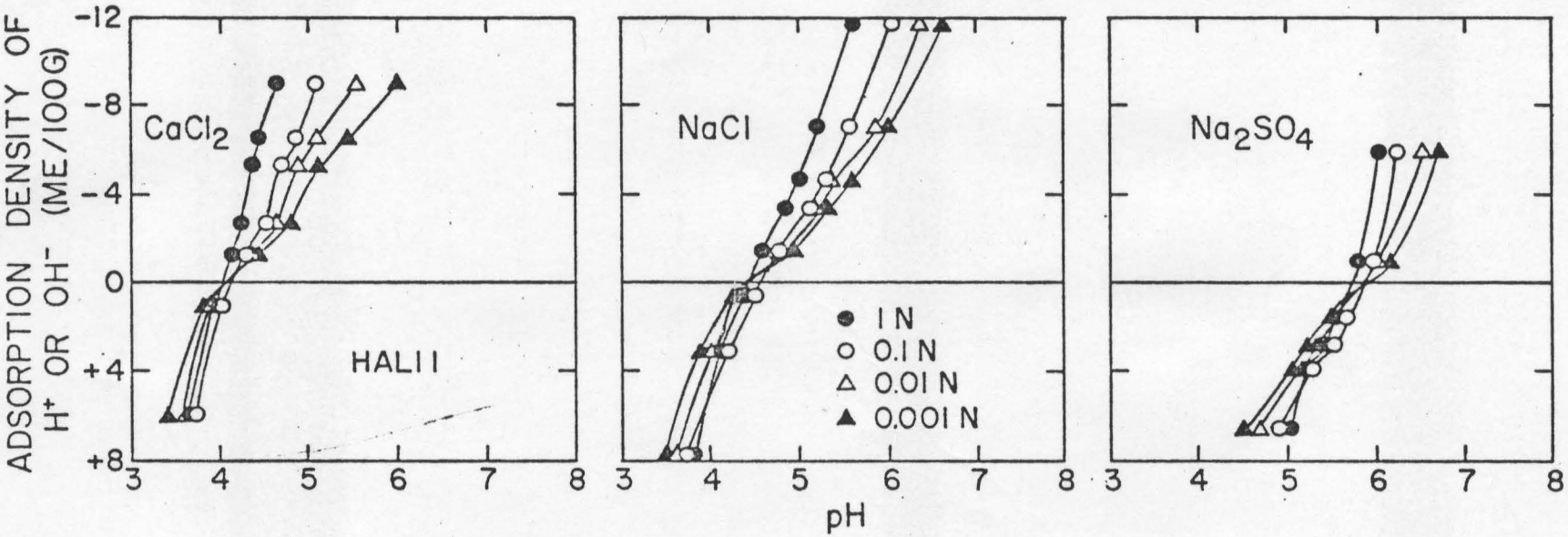

Fig. 12. The Net Electric Charge of Halii Subsoil as Determined by Potentiometric Titration

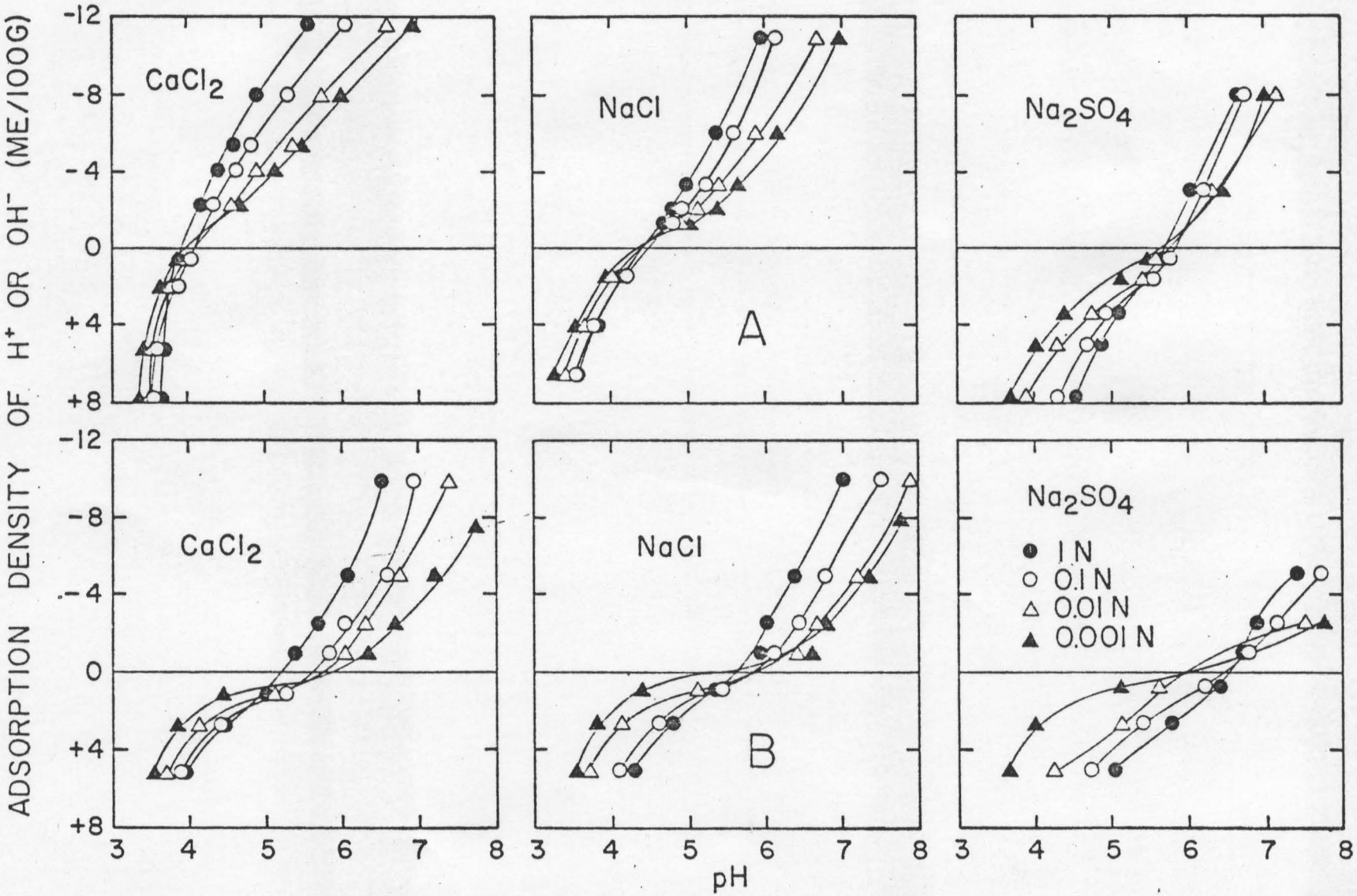

Fig. 13. The Net Electric Charge of Halii Surface (A) and Subsoil (B) as Determined by Potentiometric Titration

and smectite, and natural iron oxide. Their X-ray diffraction patterns are presented in Appendix A. The ZPC's for these minerals fall in a narrow range between 4.10 to 6.68. The potentiometric titration curves of kaolinite, in the presence of $CaCl_2$ and NaCl solutions, tend to merge when the pH values are below 2.36 and 2.49 respectively. This result is not surprising since the maximum number of positive charges created in low pH values are limited by the site of reversible charges on the kaolinite surface. No ZPC was found in the montmorillonite sample.

D. ZPC of Soils

The soils used in this study were selected so that results obtained from them might be used to predict similar data for related soils. For example, two Oxisols were chosen for careful analysis of ZPC. They were the Molokai (Typic Torrox) and the Halii (Typic Gibbsihumox) series. These soils represent end members of the spectrum of Oxisols in the State. The Molokai series is relatively low in oxide and high in kaolinite content. The Halii is for all practical purposes an oxide system, containing 2-5% SiO_2, mostly in the form of quartz. In selecting these soils for analysis, it was assumed that all Oxisols of Hawaii would possess surface colloid characteristics intermediate between the Molokai and Halii series. Figs. 14 and 13 show titration curves for the Molokai and Halii soils. Both have well defined ZPC's and the ZPC with $CaCl_2$ and Na_2SO_4 fall below and above the ZPC obtained with CaCl.

The curves for the Halii is similar to that obtained for goethite (Fig. 11), and the curves for the Molokai resemble those

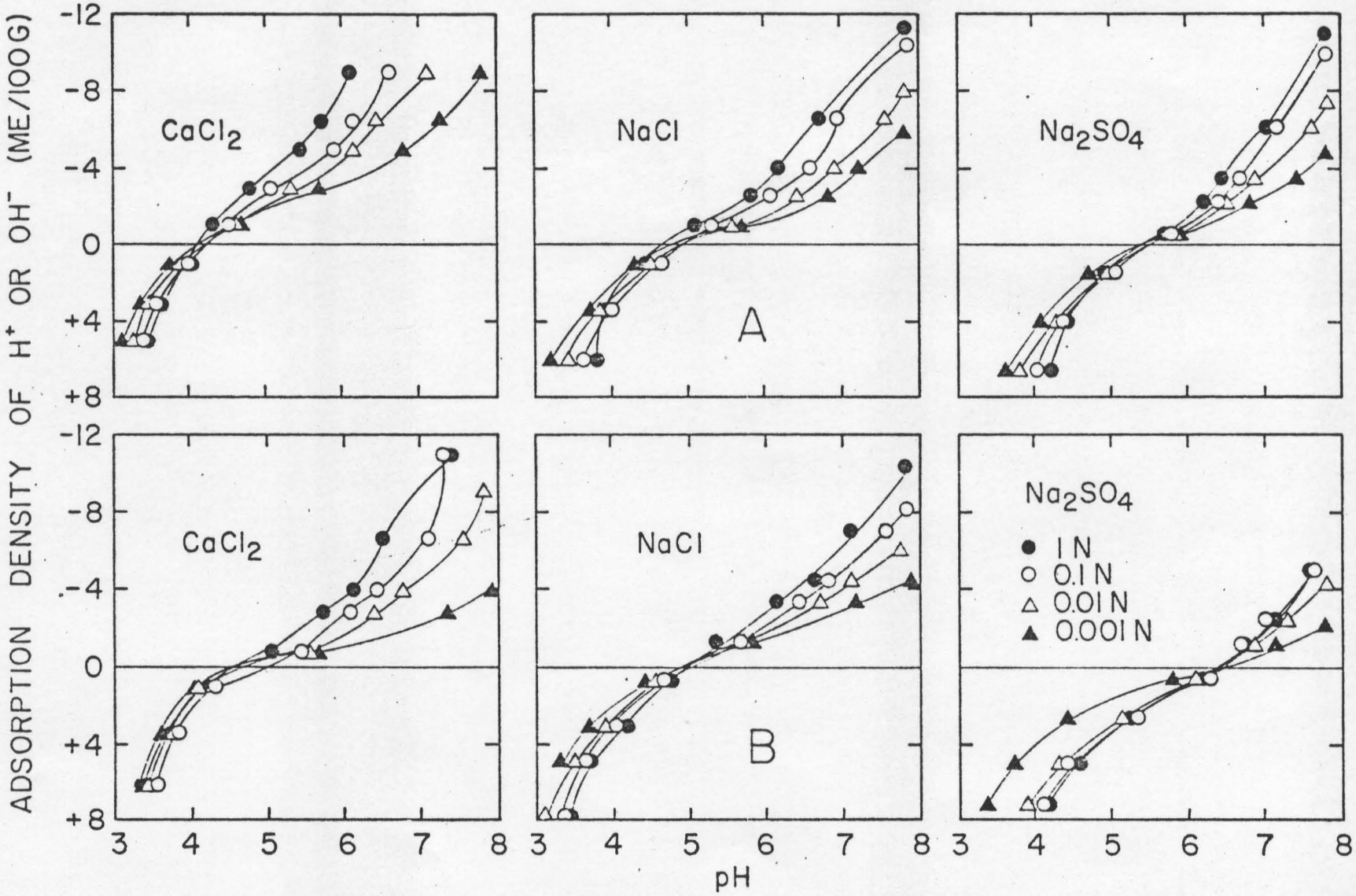

Fig. 14. The Net Electric Charge of Molokai Surface (A) and Subsoil (B) as Determined by Potentiometric Titration

of the gibbsite-halloysite mixture (Fig. 8). In both soils the ZPC's are higher in the subsoil than the top soil. This is generally attributed to the lower organic matter content of the subsoil (van Raij and Peech (1972); Uehara, et al. 1972).

The samples selected to represent soils developed from volcanic ash (Andepts) were the Waimea (Typic Eutrandepts) and the Hilo (Typic Hydrandepts) series. The Hilo series which has a high free, non-crystalline iron and aluminum oxide content gives data characteristic of oxide systems. The Waimea series which is high in non-crystalline alumino-silicate, however, gives curves which are very much like those obtained with montmorillonite. This finding strongly suggests that Eutrandepts and other less weathered Andepts contain colloids which are of the constant charge type. If the Waimea soil has large numbers of permanent charge, they are most likely due to aluminum ion in four coordination.

Soils which are classified as Dystrandepts would give titration curves intermediate between the Hilo and Waimea soils, with the Hydric Dystrandepts being more like the Hilo series and the Typic Dystrandepts being more like the Waimea. This idea can be readily tested by determining ZPC of appropriate soils in the Dystrandepts great group.

Three other soils were studied. They included the Paaloa series, a Humoxic Tropohumults; the Lualualei series, a Typic Chromusterts, and the Puna series, a Typic Tropofolists.

The Paaloa series contains a large quantity of material blown in from the continents (Juang and Uehara, 1968, Jackson et al.,

1971). It is high in quartz and mica, two minerals which do not occur naturally in soils of Hawaii, as well as anatuse, rutile, goethite, ilmenite, hematite and some kaolinite. Of the cultivated Tropohumults in the State, the Paaloa is possibly the soil most contaminated with tropospherically derived minerals. The titration curves for the Paaloa soil may be strongly influenced by quartz. While quartz possesses a ZPC, the ZPC value is near pH 3 (Tardos and Lyklema, 1969), and the Paaloa series in turn gives ZPC values more like silica than iron or aluminum oxide.

The Lualualei soil gives a family of titration curves which run parallel to each other (Fig. 19) much like the curves for Wyoming Bentonite (Fig. 10). Soils of the State which can be expected to give titration curves of this character are those that fall in the Vertisol order and some that fall in the order Mollisols. It would be interesting to see if the Waihuna series, a Typic Chromustert, but with a halloysite mineralogy, would give titration curves of the Lualualei type.

Lastly, an organic soil was examined for ZPC. The soil was the Puna series. The curves again do not intersect in as clear a fashion as the oxidic materials, but there is an indication of intersection at pH 4.5, 5.7 and 6.5 with $CaCl_2$, NaCl and Na_2SO_4 respectively. Organic matter probably occurs as free humus as in the Histosols and as compounds strongly adsorbed on inorganic colloid surface. Of the soils used in this study, the Hilo soils represents the best example of a soil in which the organic and inorganic fractions have combined to give sesquioxide-organic matter complexes.

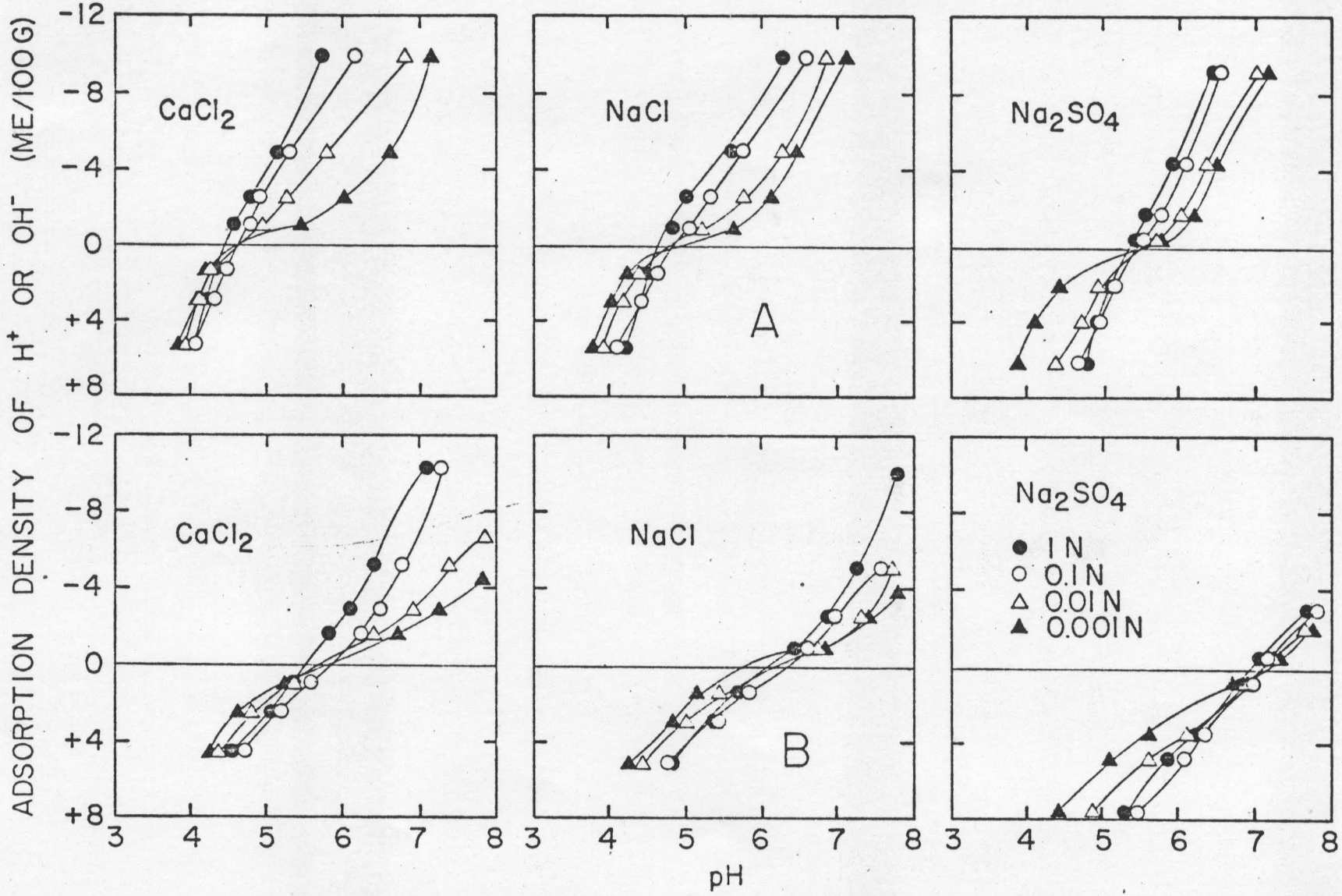

Fig. 15. The Net Electric Charge of Hilo Surface (A) and Subsoil (B) as Determined by Potentiometric Titration

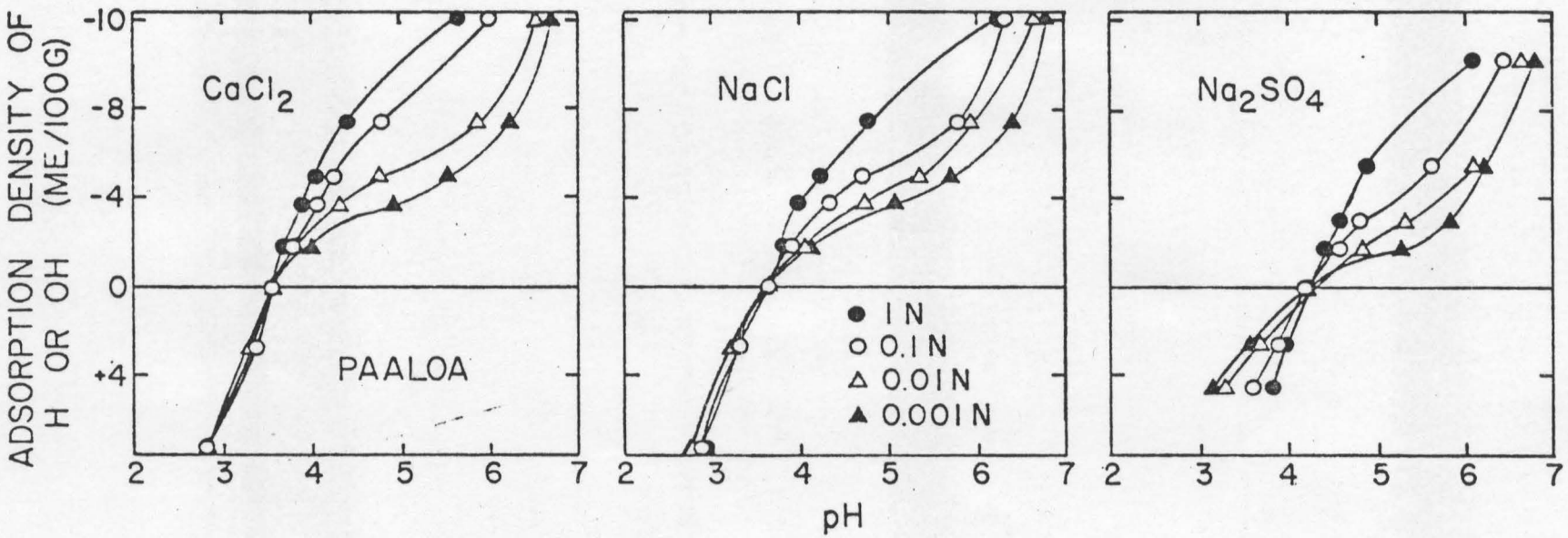

Fig. 16. The Net Electric Charge of Paaloa Soil as Determined by Potentiometric Titration

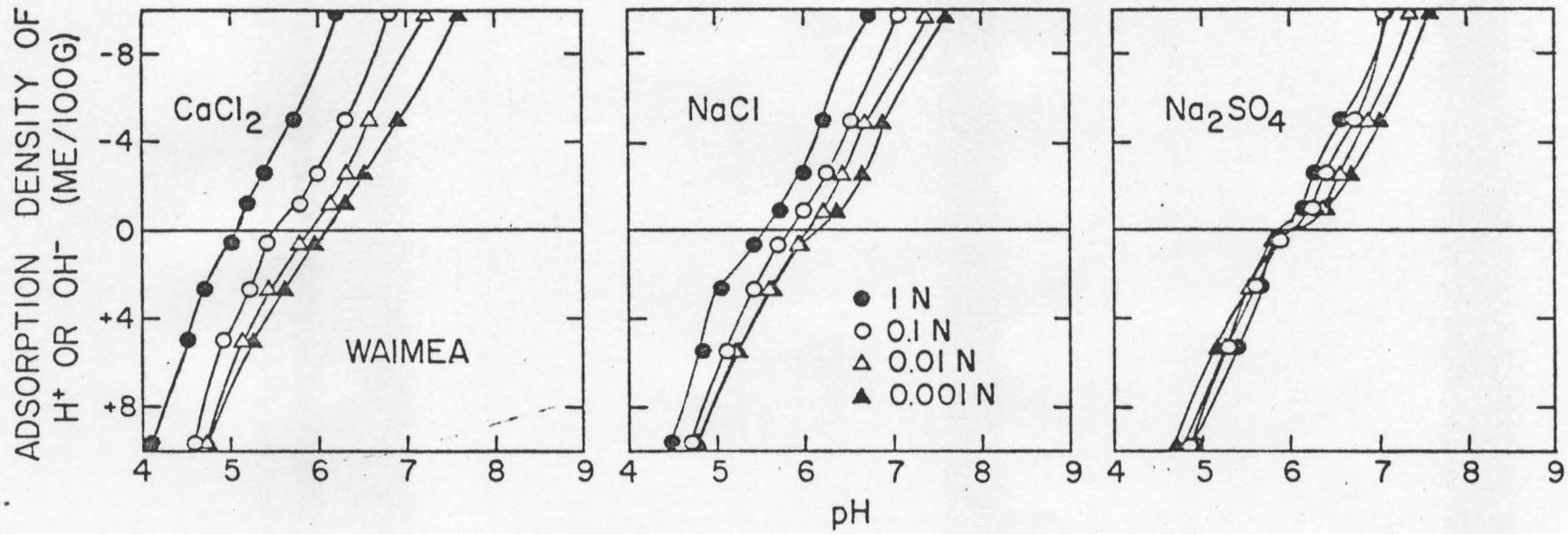

Fig. 17. The Potentiometric Titration Curves for Waimea Soil as Determined by Potentiometric Titration

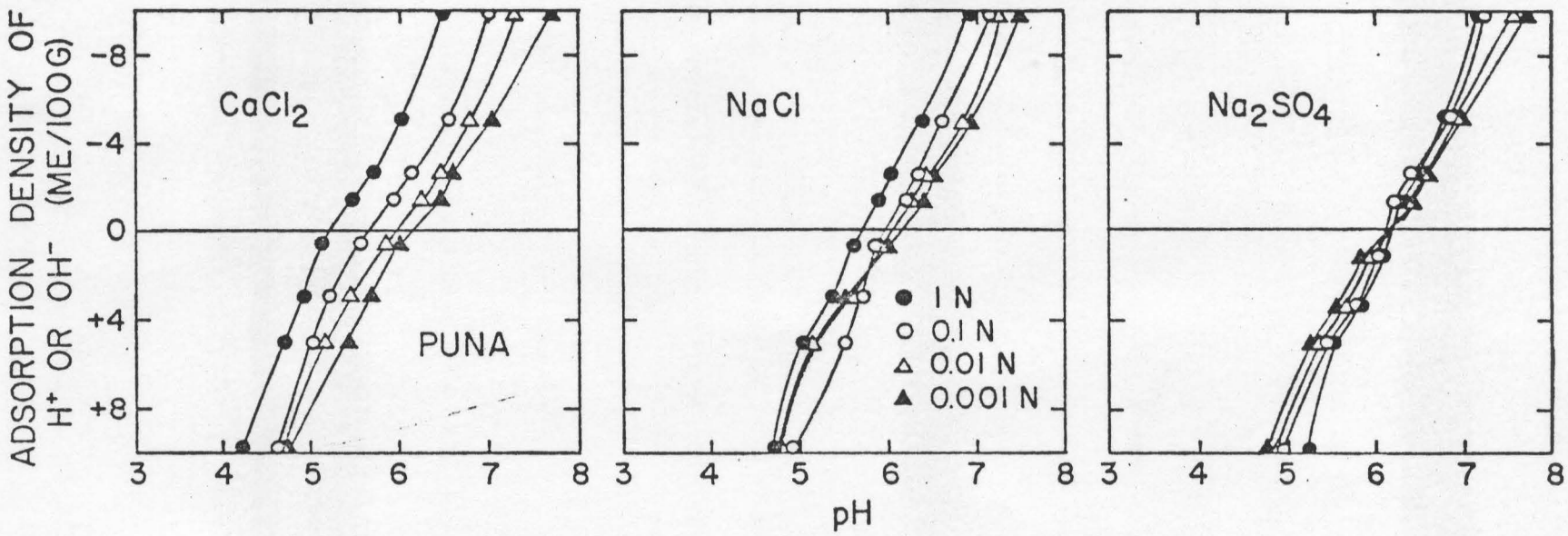

Fig. 18. The Potentiometric Titration Curves for Puna Soil as Determined by Potentiometric Titration

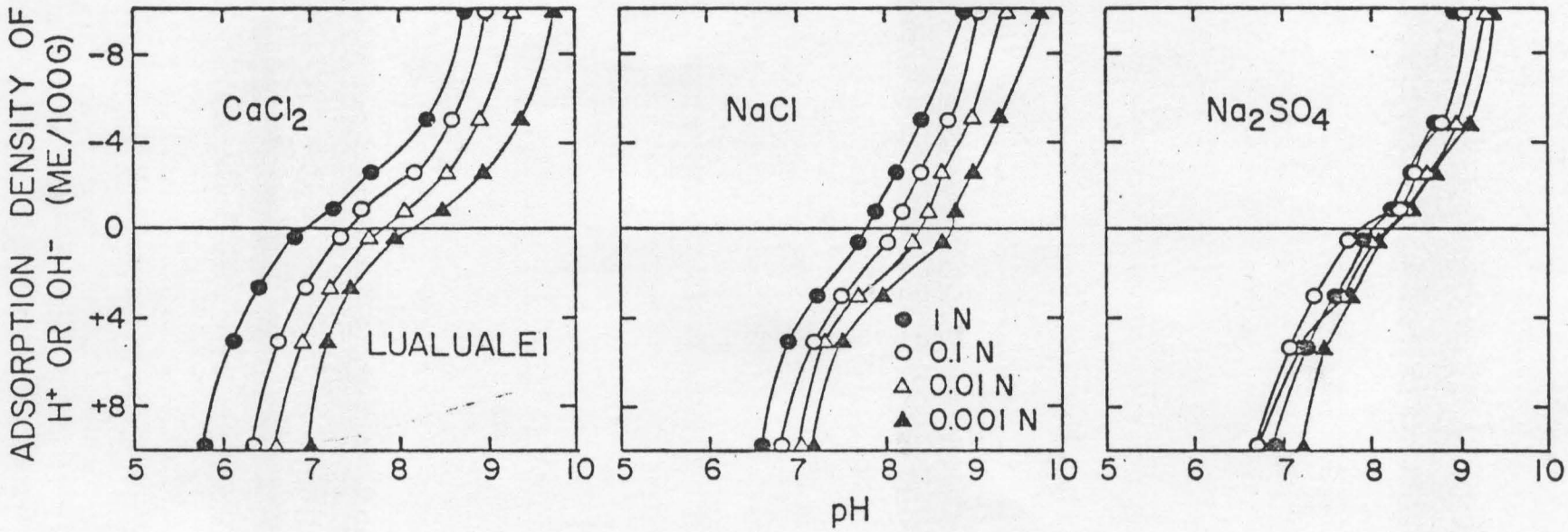

Fig. 19. The Potentiometric Titration Curves for Lualualei Soil as Determined by Potentiometric Titration

E. Zero Point of Titration

Table 4 shows that most of the samples, with the exception of the Halii and Hilo subsoils, are net negatively charged in the field. This result indicate that even in soils which are very high in sesquioxide content, the colloid are more often than not, net negatively charged.

F. σ -pH Curves in (2-1), (1-1) and (1-2) Electrolytes

In comparing Ca^{++} and Na^{+} adsorption in the presence of Cl^{-}, and Cl^{-} and SO_4^{--} adsorption in the presence of Na^{+}, it is convenient to study the σ_o -pH curves at constant electrolyte concentration. Results of Hilo, Molokai, Paaloa, and Waimea series give similar features as the Hilo soil and therefore have been omitted.

It is observed that in 10^{-3} N solutions the σ_o -pH curves of the various electrolytes merge into a single curve (Fig. 20). This suggests that the effect of ion species at low concentration is very small.

In 10^{-1} N and 10^{-2} N solutions, the titration curves for $CaCl_2$ and NaCl approach each other below the ZPC. This is to be expected because there the double layer properties are mainly determined by the Cl anion. By the same argument, the NaCl and Na_2SO_4 curves approach each other at high pH. It is also seen that the order of adsorption in 10^{-1} N and 10^{-2} N solutions is : Ca > Na; in the presence of Cl^{-}, and $SO_4^{--} > Cl^{-}$, in the presence of Na^{+}.

Based on the curves in Figure 20, one can readily see that at any given net surface charge, the change in pH with change in

Table 4. The ZPC in relation to the zero point of titration

Sample Source	Depth (inch)	Position of ZPC with respect to zero point of titration: $CaCl_2$ 1N	$CaCl_2$ 0.1N	$CaCl_2$ 0.01N	$CaCl_2$ 0.001N	NaCl 1N	NaCl 0.1N	NaCl 0.01N	NaCl 0.001N	Na_2SO_4 1N	Na_2SO_4 0.1N	Na_2SO_4 0.01N	Na_2SO_4 0.001N
Soil Samples													
Halii	0-5	0.12+	0.30+	0.51+	0.61+	0.10+	0.17+	0.28+	0.31+	0.70-	0.68-	0.88-	1.07-
Halii[a/]	0-5	0.13+	0.39+	0.48+	0.59+	0.07+	0.14+	0.23+	0.30+	0.51-	0.42-	0.50-	0.81-
Halii	24-36	0.45-	0.01-	0.23-	0.29-	0.55-	0.45-	0.47-	0.73-	1.09-	0.28-	1.29-	1.52-
Molokai	0-6	0.81+	1.12+	1.59+	1.81+	0.69+	1.02+	1.20+	1.46+	0.28+	0.40-	0.56-	0.74-
Molokai	24-36	1.04+	1.38+	1.66+	2.00+	1.10+	1.32+	1.37+	1.51+	0.02-	0.01+	0.03-	0.06-
Hilo	0-6	0.05-	0.08+	0.08+	0.15+	0.12-	0.01+	0.03+	0.04-	0.37-	0.30-	0.14-	0.47-
Hilo	25-40	0.11-	0.11+	0.19+	0.06+	0.23-	0.09-	0.12-	0.24-	0.46-	0.36-	0.42-	0.74-
Paaloa	12-24	0.23+	0.32+	0.42+	0.74+	0.10+	0.25+	0.47+	0.66+	0.13-	0.11+	0.18+	0.32+
Waimea	12-24	--	--	--	--	--	--	--	--	0.26+	0.31+	0.38+	0.41+
Puna	0-6	--	--	--	--	--	--	--	--	--	--	--	--
Lualualei	12-24	--	--	--	--	--	--	--	--	--	--	--	--
Mineral Samples													
Goethite		0.36-	0.36-	0.47-	0.60-	0.38-	0.40-	0.55-	0.58-	0.73-	0.38-	0.27-	1.18-
Gibbsite and Halloysite		0.78+	0.94+	0.95+	1.08+	0.48+	0.62+	0.78+	0.98+	0.71-	0.50-	0.53-	0.89-
Kaolinite		1.52+	1.53+	1.76+	2.10+	1.37+	1.69+	2.09+	2.39+	0.40+	0.31+	0.66+	0.96+
Smectite[b/]		--	--	--	--	--	--	--	--	--	--	--	--

Note: "+" and "-" signs indicate ZPC is located on the acid side and alkaline side of the zero point of titration respectively.

[a/] Halii soil ground to pass 100 mesh screen

[b/] 25 Upton Wyoming, Ward's Natural Science Establishment, Inc.

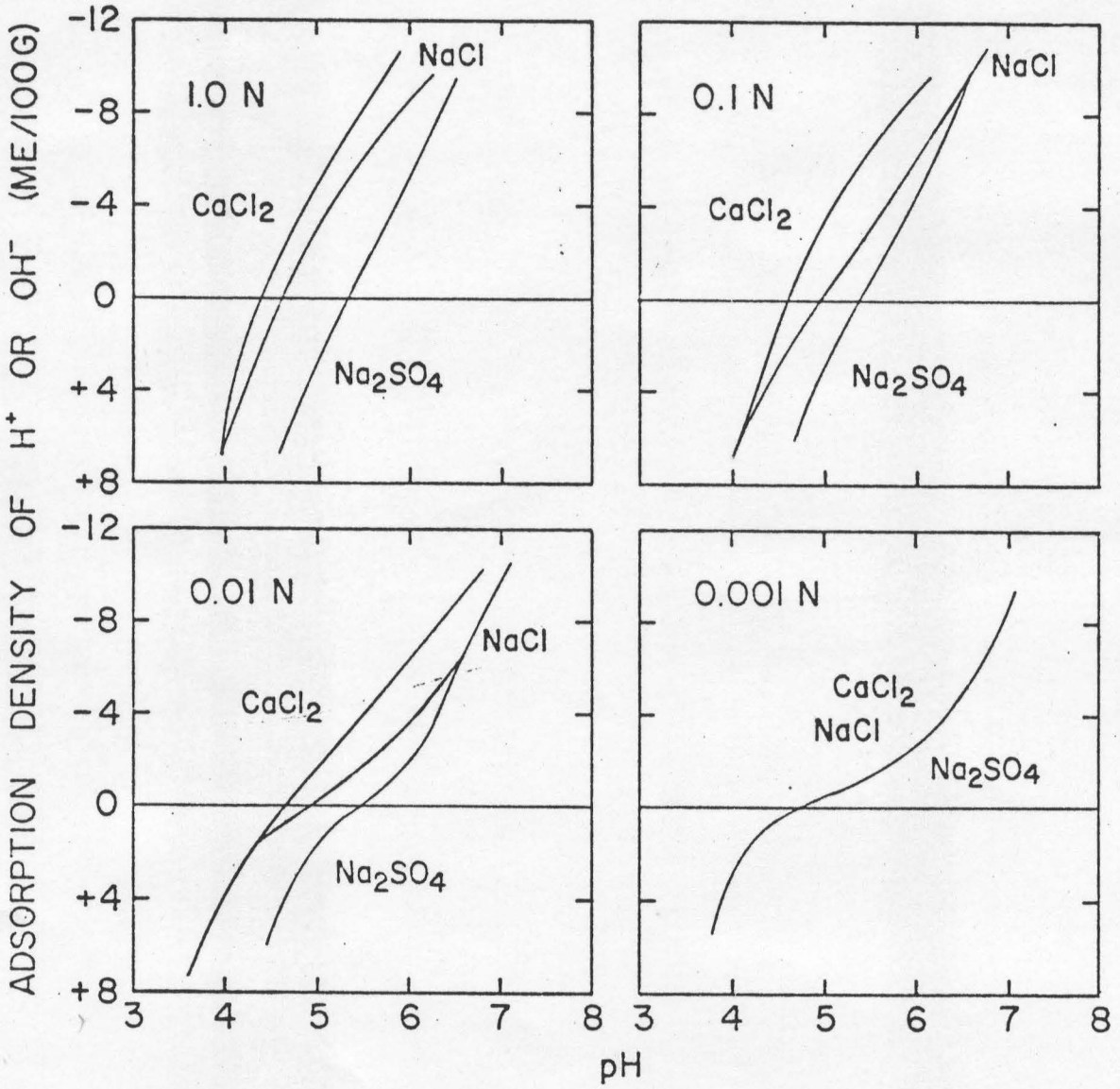

Fig. 20. The Surface Charge pH Curves of Hilo Surface Soil in the Presence of 1N, 0.1N, 0.01N and 0.001N Solutions of $CaCl_2$, NaCl and Na_2SO_4

electrolyte concentration is a negative quantity with $CaCl_2$ and a positive quantity with Na_2SO_4 relative to NaCl. The expression

$$\frac{\partial \text{ pH}}{\partial \log a_{\sigma}} = \beta$$

is the Esin-Markov Coefficient. It describes the change in pH with each ten fold change in salt activity a at constant surface charge. On the high negative side, β is -1/2 for $CaCl_2$ and -1 for NaCl (Breeuwsma and Lyklema, 1972). The results clearly show that the change in pH is much greater than -1/2 for $CaCl_2$. This is the best evidence for specific adsorption of calcium ion. The same argument applies to sulfate on the positive side of the ZPC.

In more practical terms, at a given surface charge associated with a given quantity of OH^- adsorbed ($\simeq$ OH^- added), the pH is more acid when calcium ions are present than when sodium are present. This explains why titration curves obtained with NaOH frequently underestimate the lime requirement of Oxidic soils.

G. Effect of Sorbed Phosphate on ZPC

The effect of adsorbed phosphate on the ZPC is shown in Figures 21 and 22. Titration curves of the Halii subsoil treated with 5,000 ppm and 10,000 ppm phosphorus as calcium phosphate ($CaHPO_4$) and sodium phosphate (NaH_2PO_4) differ from the untreated control sample. Adsorbed phosphate shifts the ZPC to lower values, but the shift is measurable only when phosphate is added as the sodium salt.

Breeuwsma (1973) suggests that phosphate ions act as potential determining ions and therefore would shift the ZPC to lower values.

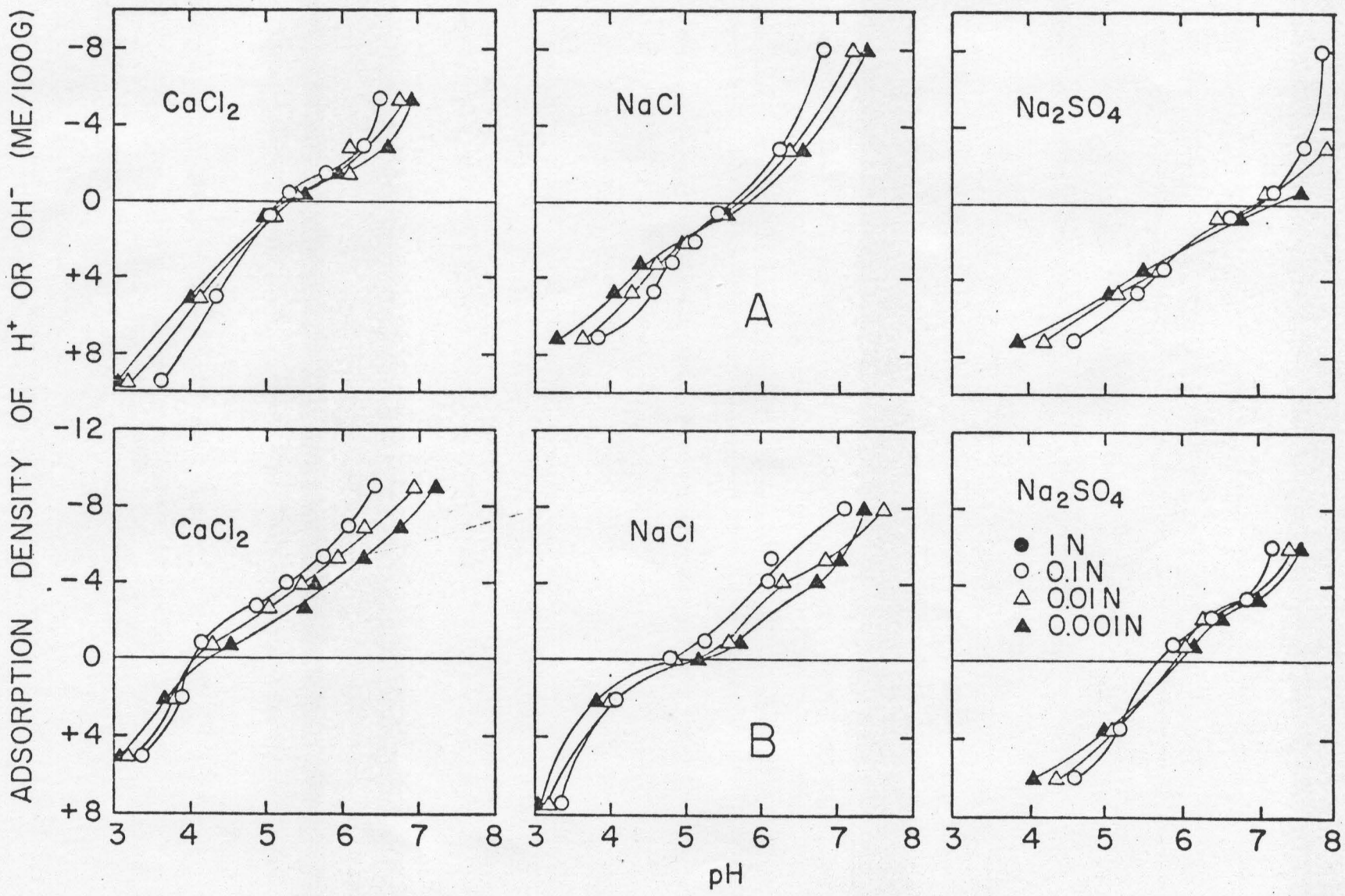

Fig. 21. The Net Electric Charge of Halii Subsoil as a Function of pH After Treatment with 5,000 ppm of P by $Ca(H_2PO_4)$ H_2O (A) and NaH_2PO_4 (B)

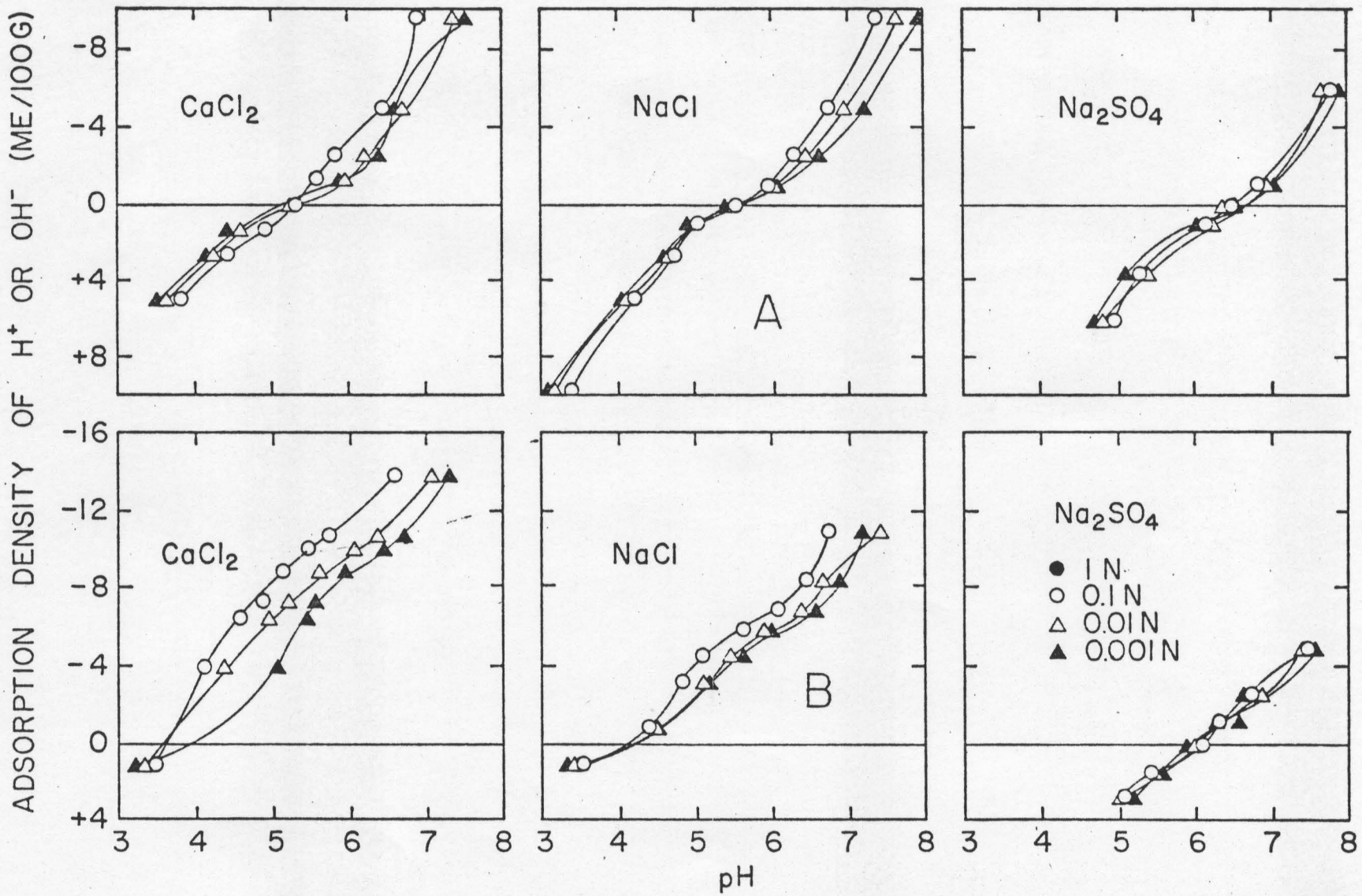

Fig. 22. The Net Electric Charge of Halii Subsoil as a Function of pH After Treated with 10,000 ppm of P as $Ca(H_2PO_4)_2\ H_2O$ (A) and NaH_2PO_4 (B)

In this case the ZPC and the isoelectric point shift in the same directions. According to Breeuwsma, sulfate ions would shift the ZPC to higher values but the isoelectric point would move to a lower value relative to the ZPC obtained when an indifferent electrolyte is used.

The difficulty arises when we apply this argument to calcium. Calcium chloride shifts the ZPC to lower values. Adsorbed phosphate also shifts the ZPC to lower values. But when both calcium and phosphate ions are added to a soil as $CaHPO_4$, the shift in the ZPC is less than the shift due to the individual ions. This may indicate that calcium is specifically adsorbed (adsorbed in the compact layer) on oxide surface, but calcium may become a potential determining ion when the oxide surface is phosphated.

Mekaru and Uehara (1972) have shown that adsorbed phosphate increases cation exchange capacity. Ayres and Hagihara (1953) and Syed-Fadzil (1972) have shown in leaching studies that phosphate increases cation retention and therefore reduces leaching losses of cationic nutrients. These observations are consistent with the shift in ZPC to lower pH when phosphate ions are adsorbed.

CONCLUSION AND IMPLICATION OF RESULTS

The result show that many, if not most, of the soils in the State contain minerals which can be treated as constant potential colloids. Soils which are predominantly montmorillonitic (Smectite) are exceptions. Another soil material which seem to behave as constant charge colloid is the material in the Waimea soil which is predominantly non-crystalline. The absence of a well defined ZPC in the Waimea soil suggests that in this soil, aluminum is four coordinated and not eight coordinated as in allophane.

In soils with constant potential colloids or soils which are often described as having pH dependent charge, the net surface charge and therefore the cation exchange capacity, can be managed. It can be managed by changing soil pH or through addition of fertilizers of ammendments which contain ions which are specifically adsorbed or ions which act as potential determining ions.

The results further indicate that the low cation exchange capacities of oxidic soils of the tropics can be increased by treatment with soil ammendments. The strong adsorptive capacity of sesquioxides for anions--a feature which is often considered as undesirable--is in fact the redeeming feature of oxidic soils. Anion adsorption will probably be used as a major means to increase soil cation exchange capacity in these soils.

The results of this study do not only apply to oxidic soils of the tropics, but to any soil which contain appreciable quantities of clay which behave as constant potential colloids.

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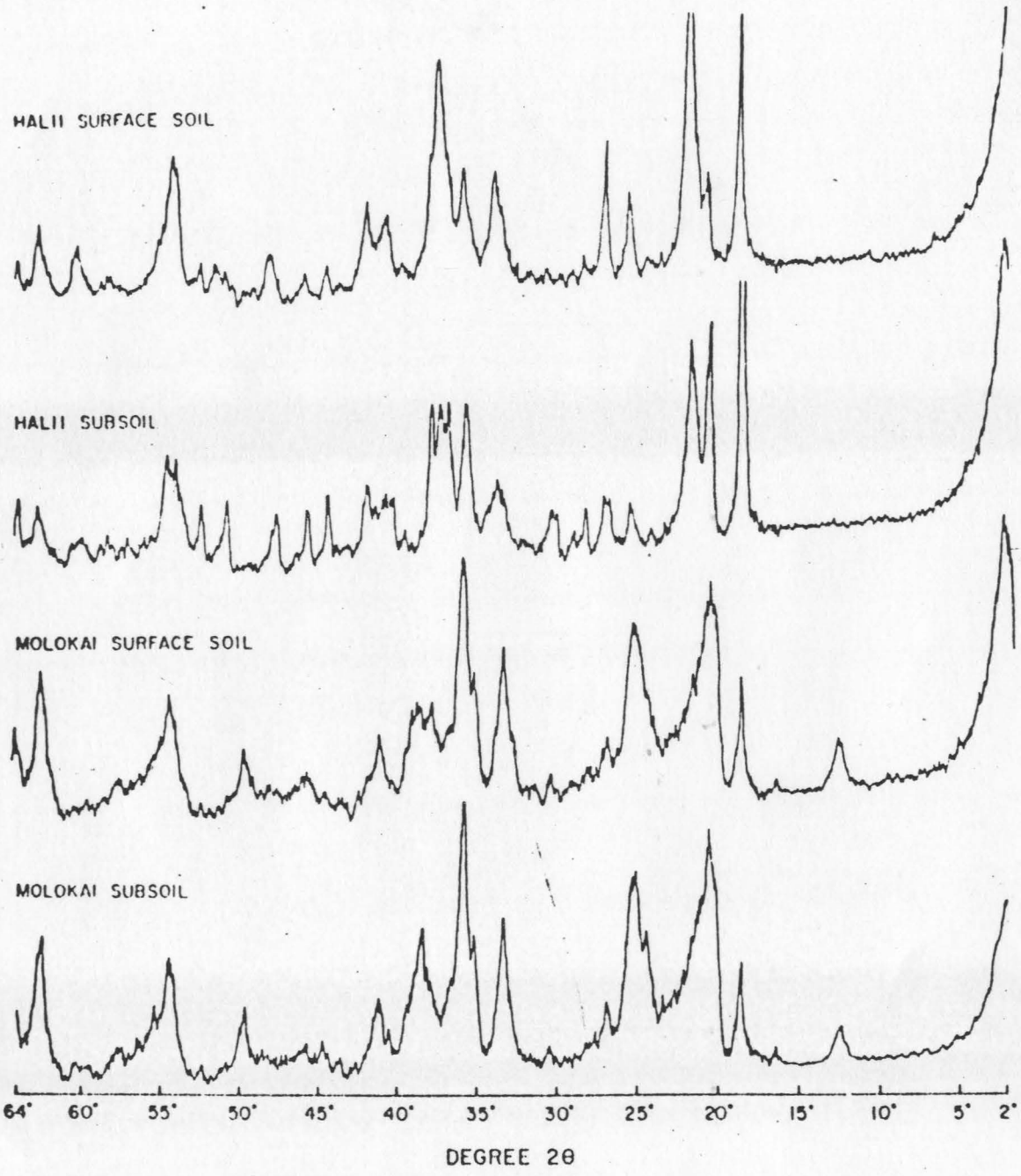
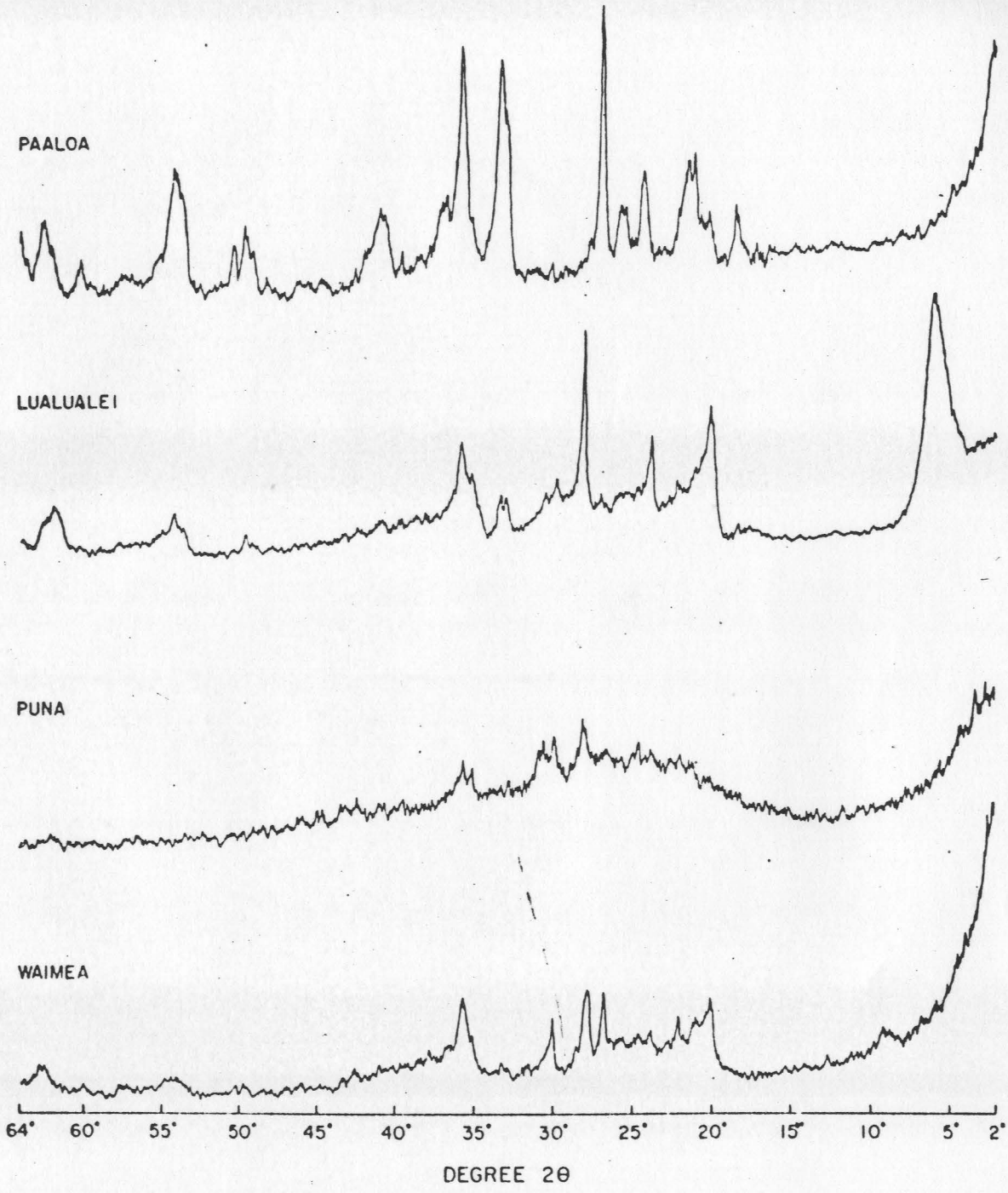
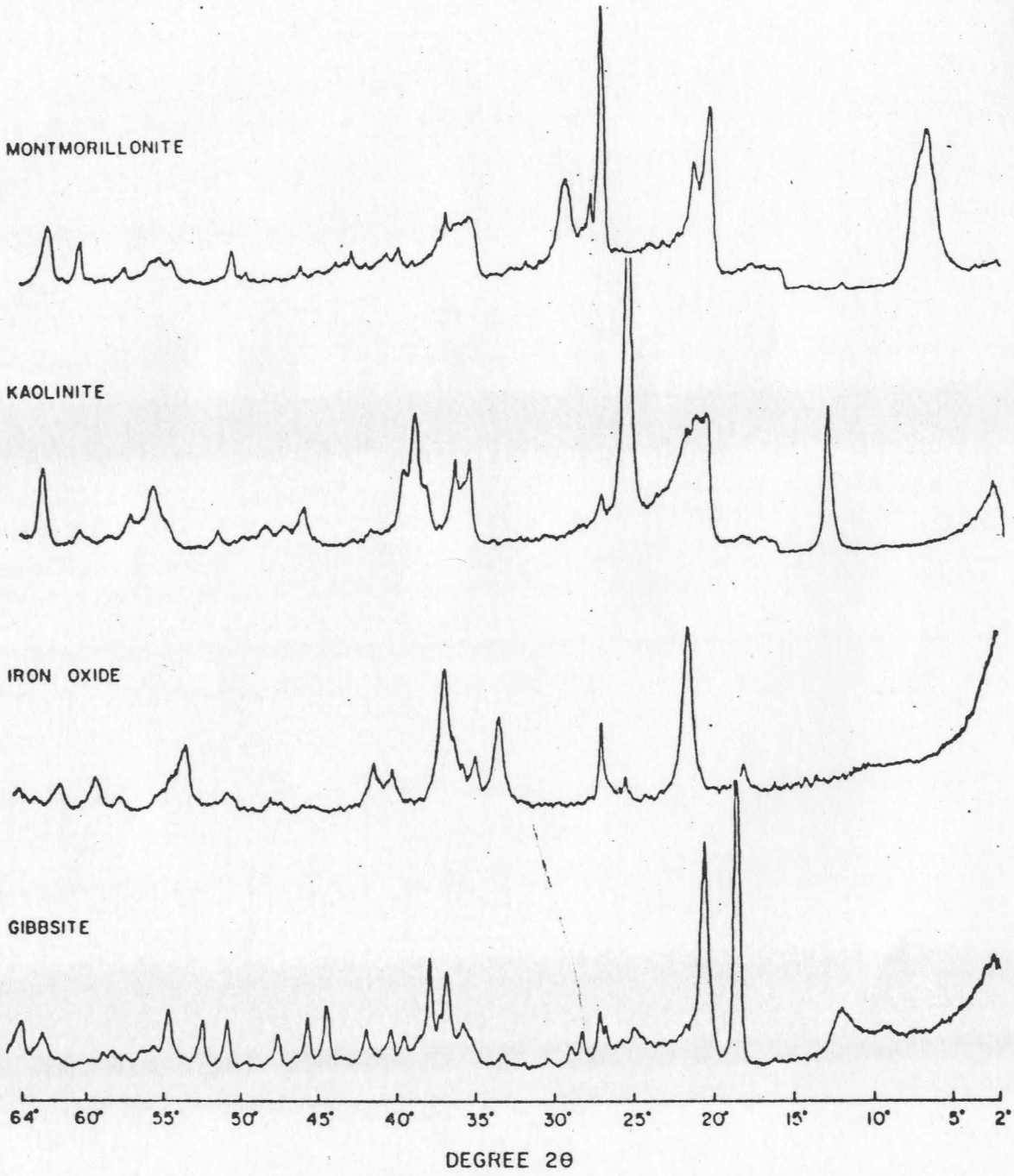
APPENDIX A

X-ray Diffractograms of Powdered Soil and Mineral Samples

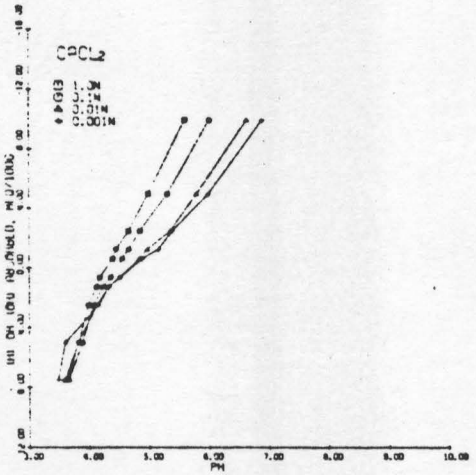

HALII SURFACE SOIL
HALII SUBSOIL
MOLOKAI SURFACE SOIL
MOLOKAI SUBSOIL
64° 60° 55° 50° 45° 40° 35° 30° 25° 20° 15° 10° 5° 2°
DEGREE 2θ

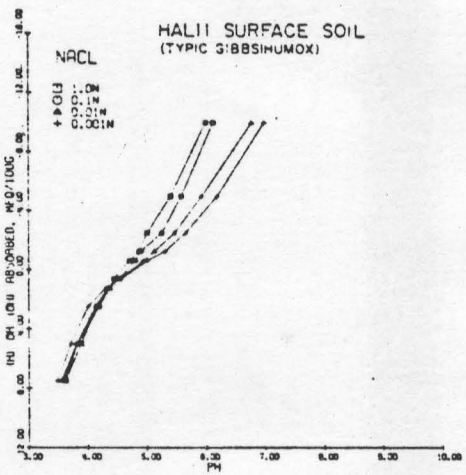

PAALOA
LUALUALEI
PUNA
WAIMEA
64° 60° 55° 50° 45° 40° 35° 30° 25° 20° 15° 10° 5° 2°
DEGREE 2θ

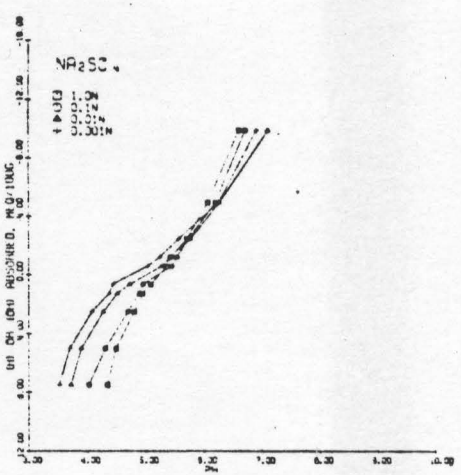

MONTMORILLONITE
KAOLINITE
IRON OXIDE
GIBBSITE
64° 60° 55° 50° 45° 40° 35° 30° 25° 20° 15° 10° 5° 2°
DEGREE 2θ

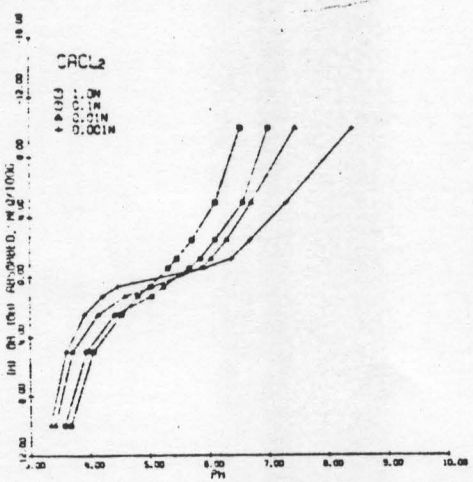
APPENDIX B

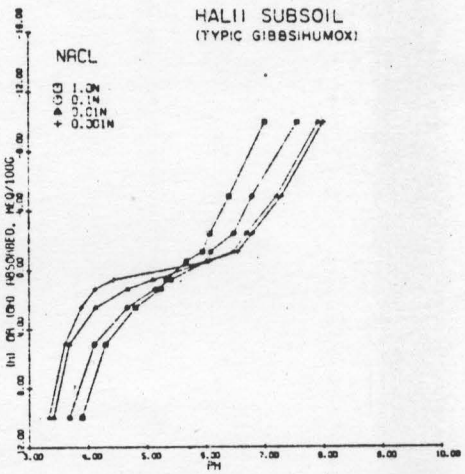
Computer Plots of Adsorbed H^+ or OH^- Versus pH for Various Soil and Mineral Samples

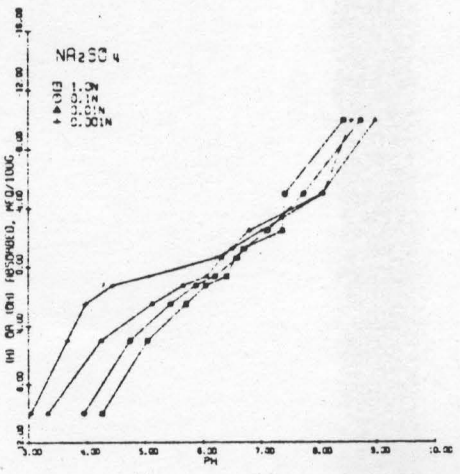

CACL2
1.0M
0.1M
0.01M
0.001M
PH

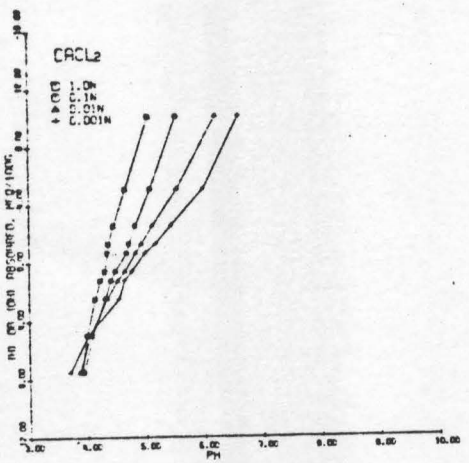

HALII SURFACE SOIL
(TYPIC GIBBSIHUMOX)
NACL
1.0M
0.1M
0.01M
0.001M
PH

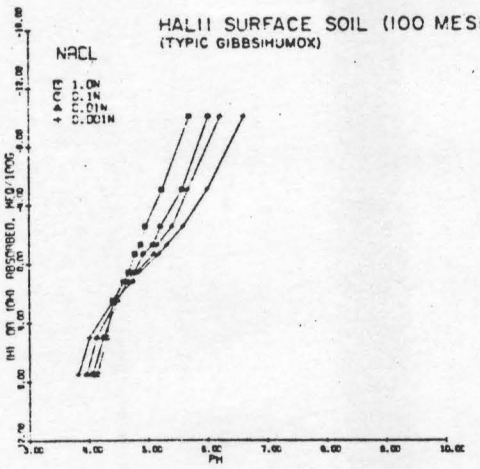

NA2SO4
1.0M
0.1M
0.01M
0.001M
PH

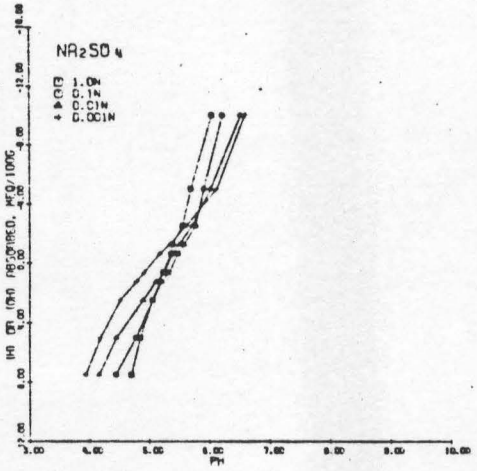

CACL2
1.0M
0.1M
0.01M
0.001M
PH

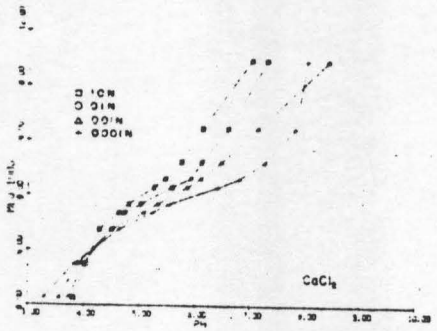

HALII SUBSOIL
(TYPIC GIBBSIHUMOX)
NACL
1.0M
0.1M
0.01M
0.001M
PH

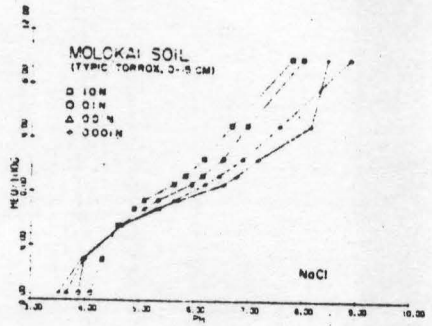

NA2SO4
1.0M
0.1M
0.01M
0.001M
PH

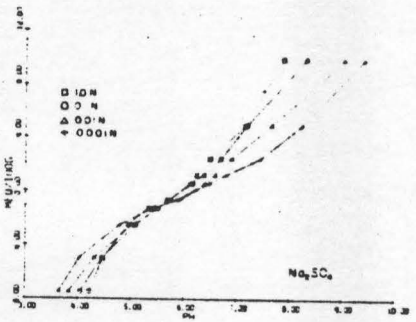

CACL2
1.0N
0.1N
0.01N
0.001N
PH

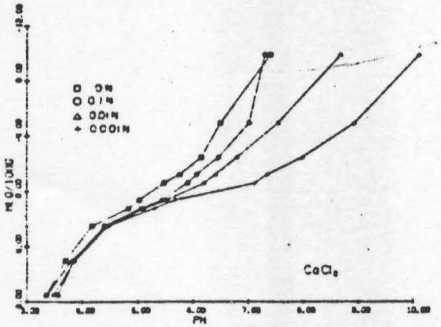

HALII SURFACE SOIL (100 MESH)
(TYPIC GIBBSIHUMOX)
NACL
1.0N
0.1N
0.01N
0.001N
PH

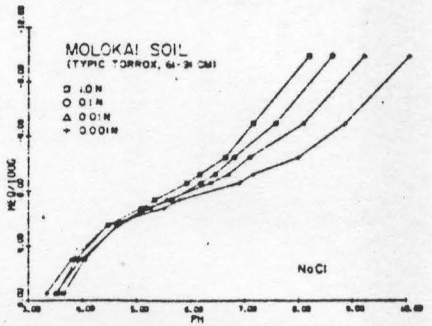

NA2SO4
1.0N
0.1N
0.01N
0.001N
PH

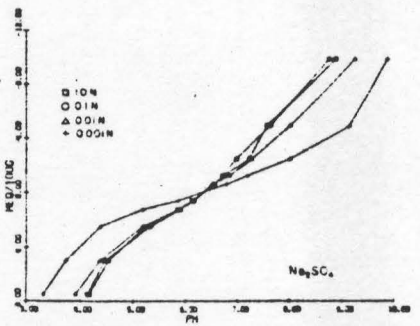

□ 1.0 N
○ 0.1 N
△ 0.01 N
+ 0.001 N
$CaCl_2$

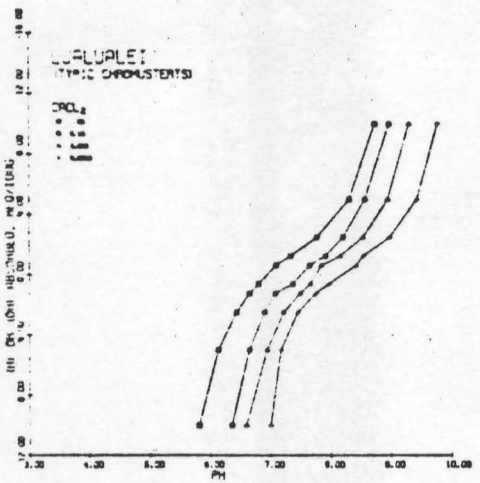

MOLOKAI SOIL
□ 1.0 N
○ 0.1 N
△ 0.01 N
+ 0.001 N
NaCl

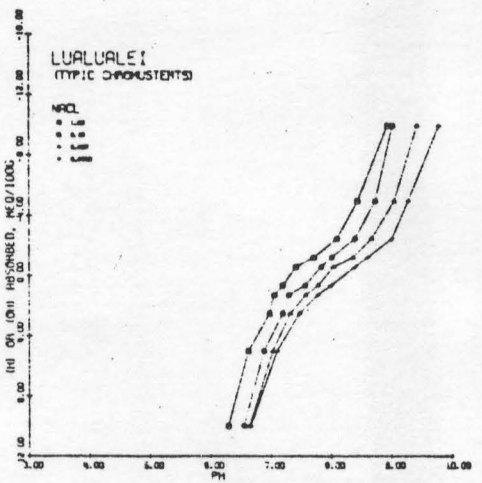

□ 1.0 N
○ 0.1 N
△ 0.01 N
+ 0.001 N
Na_2SO_4

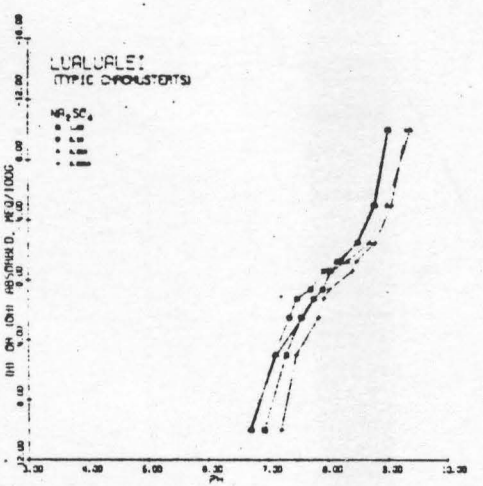

□ 1.0 N
○ 0.1 N
△ 0.01 N
+ 0.001 N
$CaCl_2$

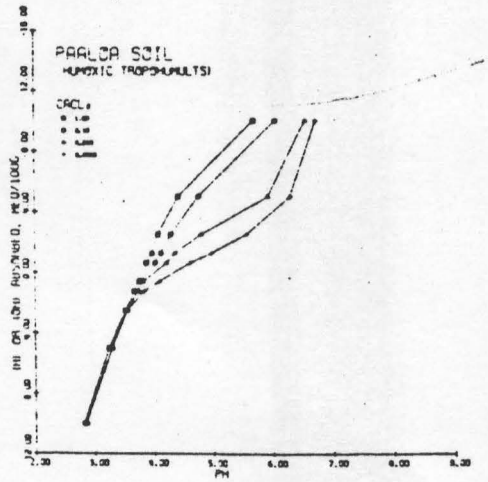

MOLOKAI SOIL
□ 1.0 N
○ 0.1 N
△ 0.01 N
+ 0.001 N
NaCl


□ 1.0 N
○ 0.1 N
△ 0.01 N
+ 0.001 N
Na_2SO_4


LUALUALEI
(TYPIC CHROMUSTERTS)
CaCl2
PH


LUALUALEI
(TYPIC CHROMUSTERTS)
NaCl
PH


LUALUALEI
(TYPIC CHROMUSTERTS)
Na2SO4
PH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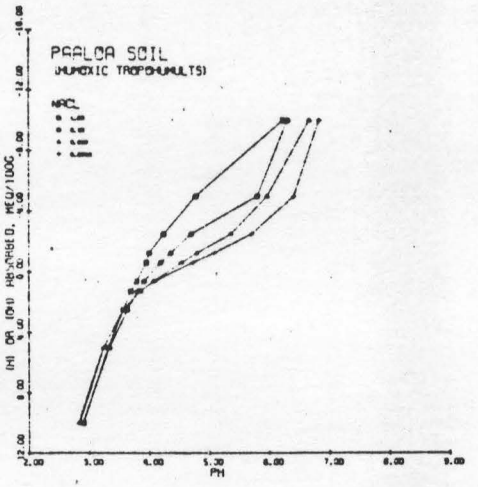
(HUMOXIC TROPUDULTS)
CaCl2
PH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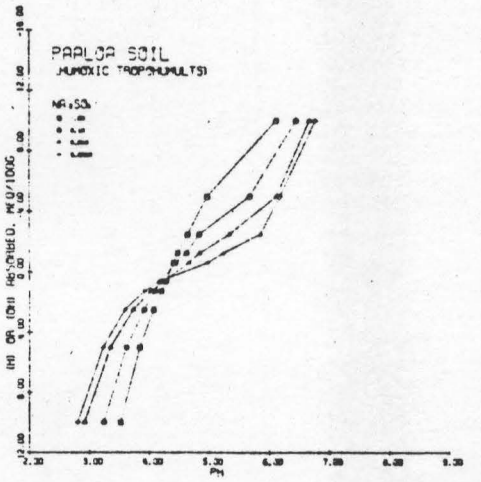
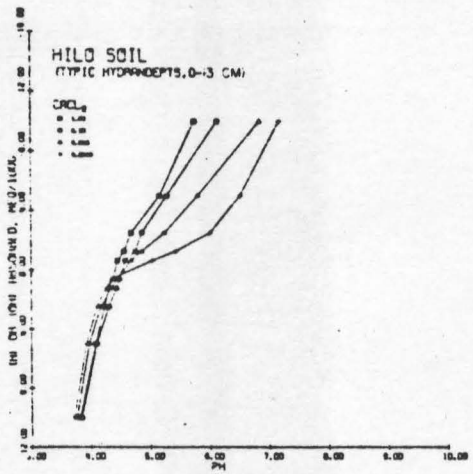
(HUMOXIC TROPUDULTS)
NaCl
PH


PAALOA SOIL
(HUMOXIC TROPUDULTS)
Na2SO4
PH


HILO SOIL
(TYPIC HYDRANDEPTS,0-13 CM)
CACL2
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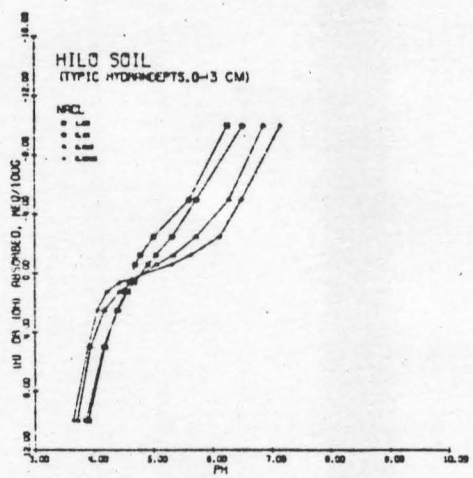
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(TYPIC HYDRANDEPTS,0-13 CM)
NACL
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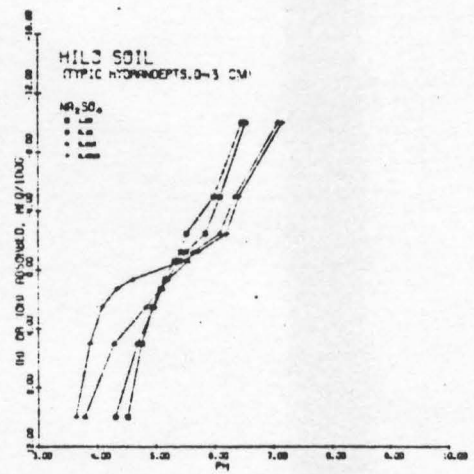
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(TYPIC HYDRANDEPTS,0-13 CM)
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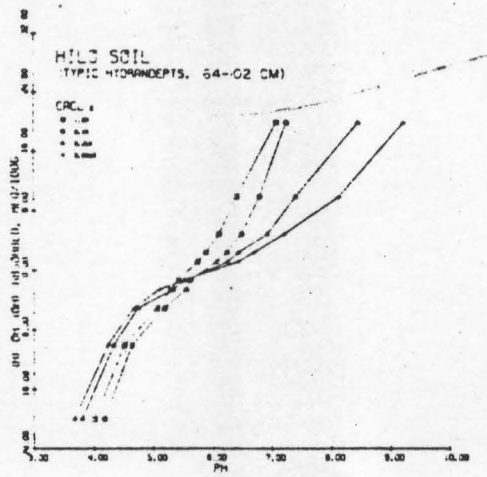
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(TYPIC HYDRANDEPTS, 64-02 CM)
CACL2
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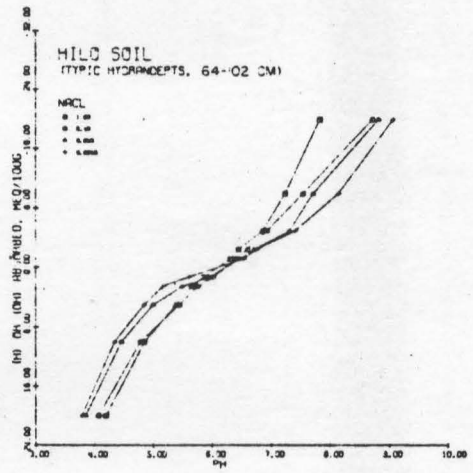
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(TYPIC HYDRANDEPTS, 64-02 CM)
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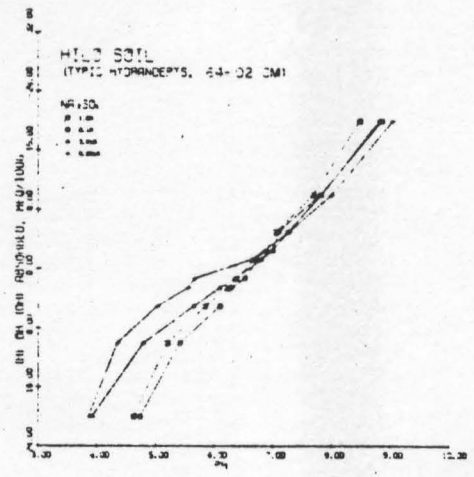
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(TYPIC HYDRANDEPTS, 64-02 CM)
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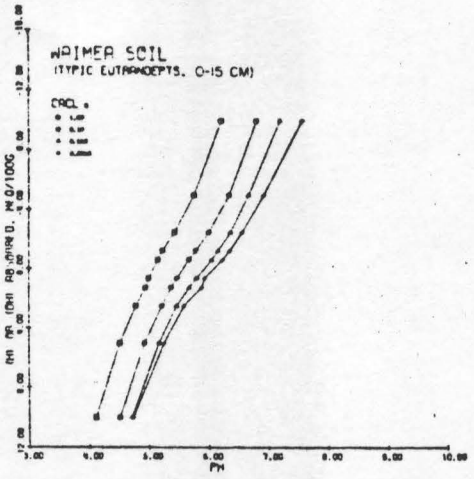
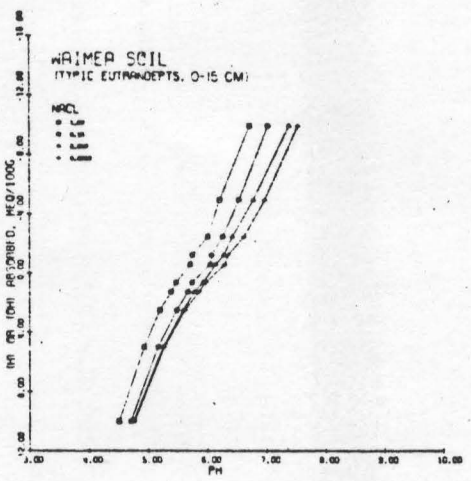

WAIMEA SOIL
(TYPIC EUTRANDEPTS, 0-15 CM)
CACL2
PH


WAIMEA SOIL
(TYPIC EUTRANDEPTS, 0-15 CM)
NACL
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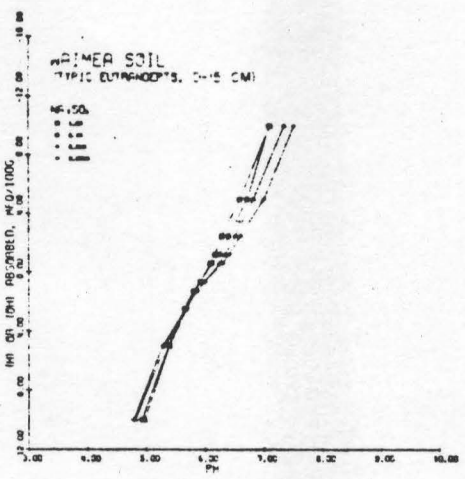
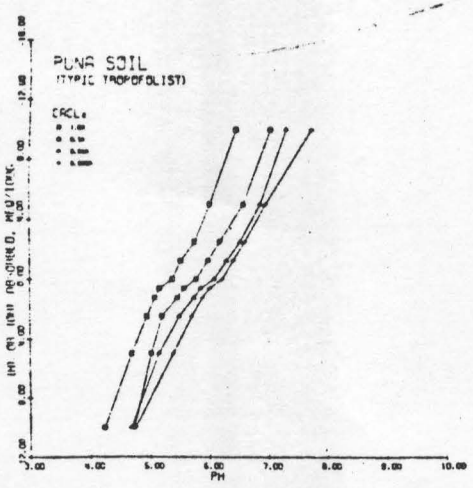
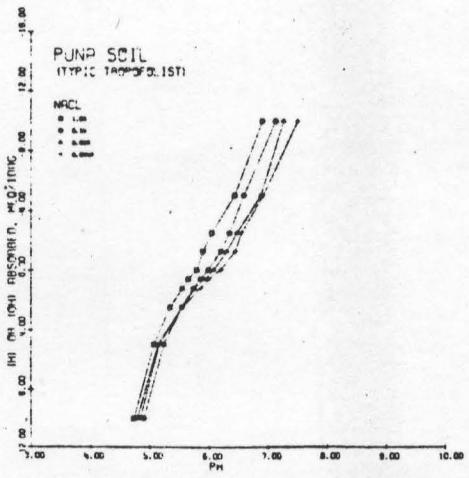
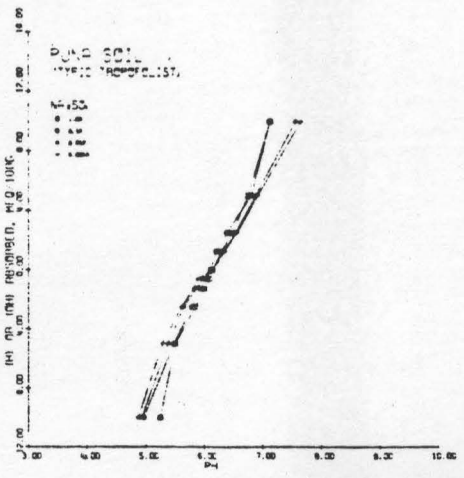
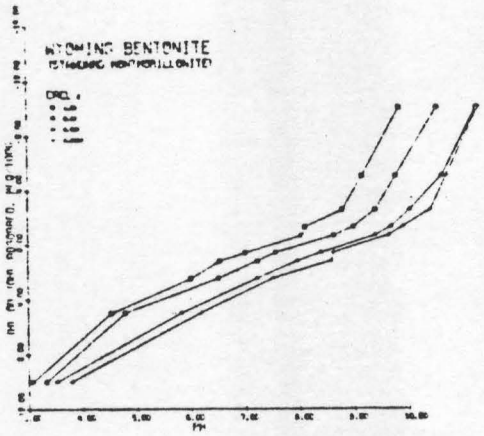
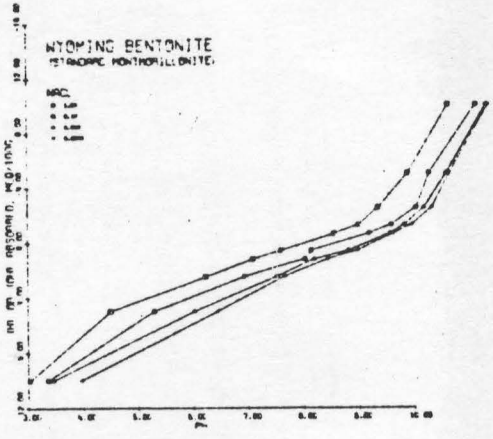

WAIMEA SOIL
PH

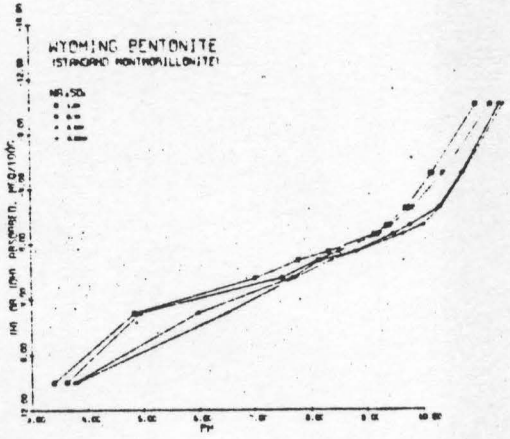

PUNA SOIL
(TYPIC TROPOFOLIST)
CACL2
PH

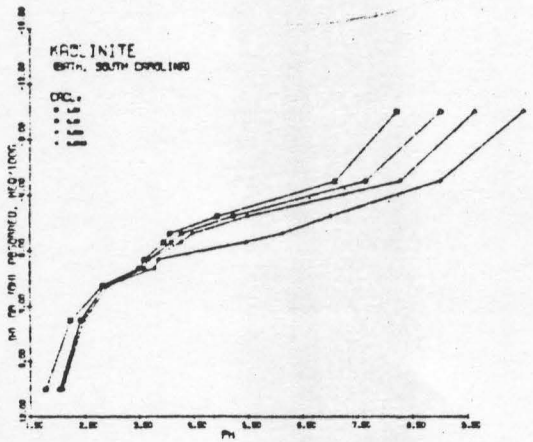

PUNA SOIL
(TYPIC TROPOFOLIST)
NACL
PH

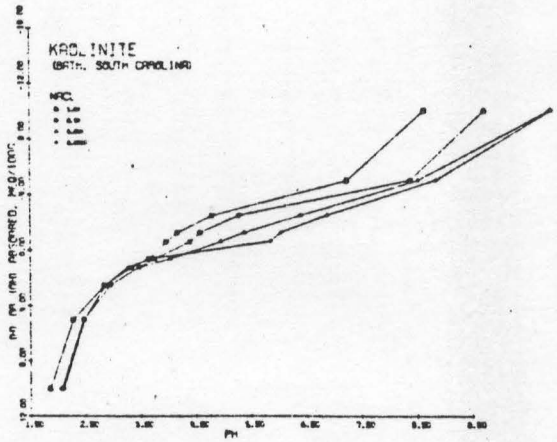

PUNA SOIL
PH


WYOMING BENTONITE
(STANDARD MONTMORILLONITE)
ORC.


WYOMING BENTONITE
(STANDARD MONTMORILLONITE)
NRC.


WYOMING BENTONITE
(STANDARD MONTMORILLONITE)
NR+SD.


KAOLINITE
(BATH, SOUTH CAROLINA)
ORC.


KAOLINITE
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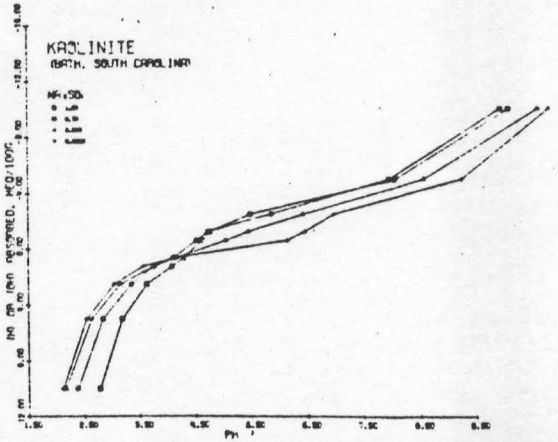
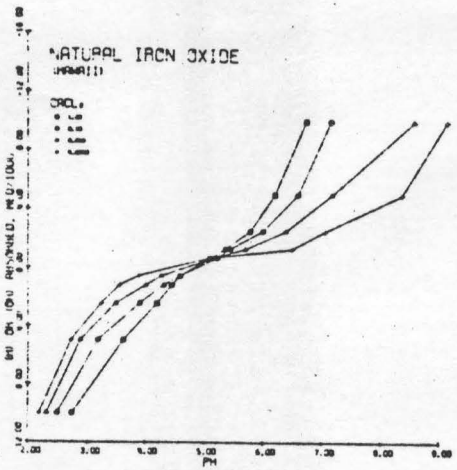
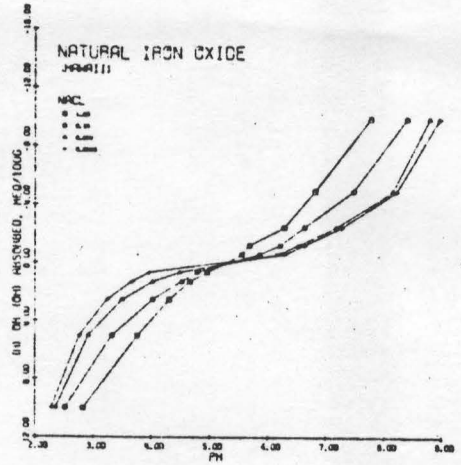

KAOLINITE
(BATH, SOUTH CAROLINA)
NR+SD.


NATURAL IRON OXIDE
HAWAII
CACL2
PH


NATURAL IRON OXIDE
HAWAII
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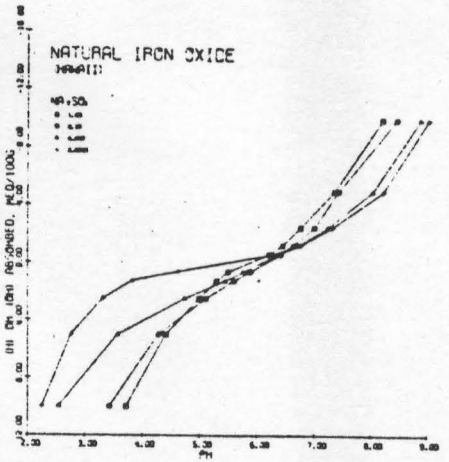
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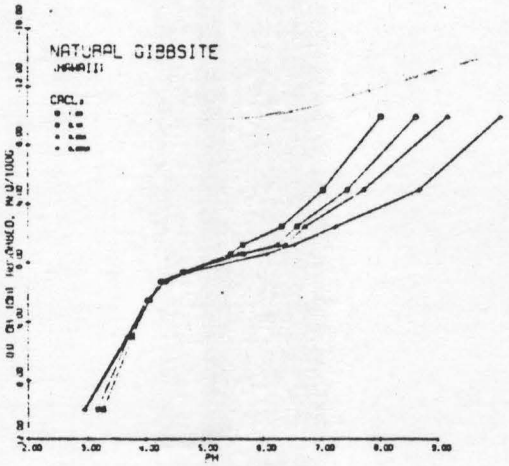
NATURAL GIBBSITE
HAWAII
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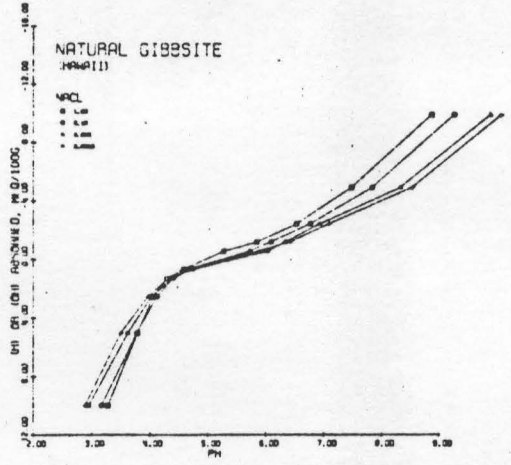
NATURAL GIBBSITE
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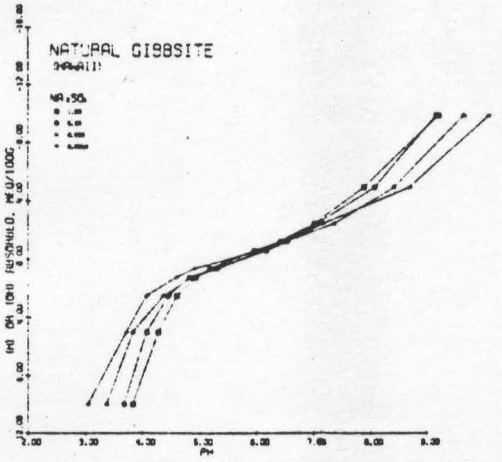
NATURAL GIBBSITE
HAWAII
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